US010326161B2

(12) **United States Patent**
Ihara et al.

(10) **Patent No.: US 10,326,161 B2**
(45) **Date of Patent: Jun. 18, 2019**

(54) **SECONDARY BATTERY, BATTERY PACK, ELECTRIC VEHICLE, ELECTRIC POWER STORAGE SYSTEM, ELECTRIC POWER TOOL, AND ELECTRONIC APPARATUS**

(71) Applicant: **Murata Manufacturing Co., Ltd.**, Kyoto (JP)

(72) Inventors: **Masayuki Ihara**, Fukushima (JP); **Tadahiko Kubota**, Kanagawa (JP)

(73) Assignee: **Murata Manufacturing Co., Ltd.**, Kyoto (JP)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 432 days.

(21) Appl. No.: **13/856,907**

(22) Filed: **Apr. 4, 2013**

(65) **Prior Publication Data**

US 2013/0273406 A1 Oct. 17, 2013

(30) **Foreign Application Priority Data**

Apr. 16, 2012 (JP) 2012-092994

(51) **Int. Cl.**
H01M 10/00 (2006.01)
H01M 10/0525 (2010.01)
(Continued)

(52) **U.S. Cl.**
CPC ***H01M 10/0525*** (2013.01); ***H01M 2/14*** (2013.01); ***H01M 10/0564*** (2013.01);
(Continued)

(58) **Field of Classification Search**
CPC H01M 10/0525; H01M 2/14; H01M 10/0567; H01M 10/0564; Y02T 10/7011; Y02E 60/122
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

2008/0311478 A1* 12/2008 Onuki H01M 10/052 429/231.95
2009/0017386 A1 1/2009 Xu et al.
(Continued)

FOREIGN PATENT DOCUMENTS

CN 101160683 4/2008
CN 101454938 6/2009
(Continued)

OTHER PUBLICATIONS

Notification of the First Office Action issued in connection with PRC Patent Application No. 2013101322671, dated Jan. 28, 2015. (42 pages).

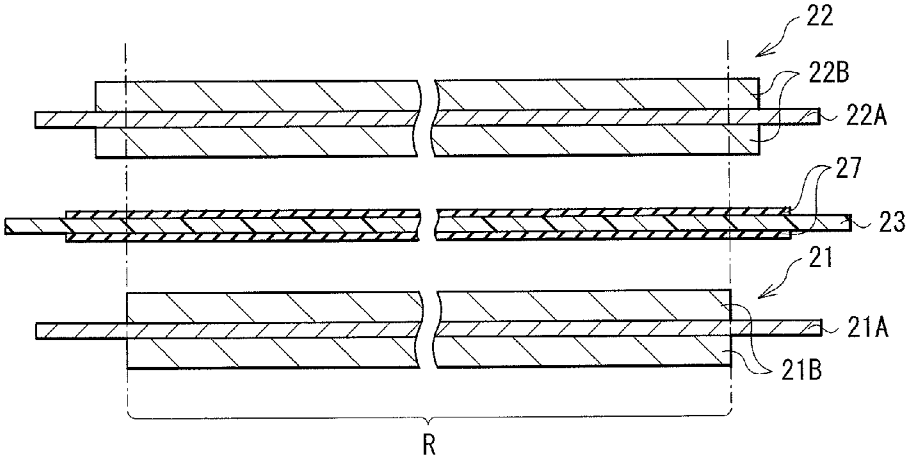
(Continued)

Primary Examiner — Cynthia H Kelly
Assistant Examiner — Monique M Wills
(74) *Attorney, Agent, or Firm* — K&L Gates LLP

(57) **ABSTRACT**

A secondary battery includes: a cathode and an anode that are opposed to each other with a separator in between; and an electrolytic solution. The cathode includes a cathode active material layer on a cathode current collector. The anode includes an anode active material layer on an anode current collector. A heat-resistant layer is provided at least in a region in which the cathode active material layer and the anode active material layer are opposed to each other between the cathode and the anode. The heat-resistant layer includes a material having a higher melting point or higher decomposition temperature than a melting point or decomposition temperature of the separator. The electrolytic solution includes an unsaturated cyclic ester carbonate.

16 Claims, 11 Drawing Sheets



(51) **Int. Cl.**

H01M 10/0564	(2010.01)
H01M 2/14	(2006.01)
H01M 10/0567	(2010.01)
H01M 10/0569	(2010.01)

(52) **U.S. Cl.**

CPC ... ***H01M 10/0567*** (2013.01); ***H01M 10/0569*** (2013.01); *Y02E 60/122* (2013.01); *Y02T 10/7011* (2013.01)

(56) **References Cited**

U.S. PATENT DOCUMENTS

2009/0226813	A1*	9/2009	Takita	B01D 67/0083 429/247
2010/0068612	A1*	3/2010	Nishikawa	H01M 2/145 429/129
2010/0069596	A1*	3/2010	Kimishima	B01D 67/002 526/352
2010/0099018	A1*	4/2010	Kawase	H01M 4/485 429/105
2010/0151310	A1*	6/2010	Takita	B01D 67/0074 429/145
2010/0247980	A1*	9/2010	Jang	H01M 2/34 429/10
2011/0033743	A1*	2/2011	Lee	H01M 2/1653 429/145
2011/0274987	A1*	11/2011	Ihara	H01M 10/052 429/337
2012/0015228	A1*	1/2012	Yoon	H01M 2/162 429/144
2012/0308872	A1*	12/2012	Huang	H01M 2/145 429/149

FOREIGN PATENT DOCUMENTS

CN	102362385	2/2012
CN	102394282	3/2012
JP	07-282849	10/1995
JP	10-050287	2/1998
JP	10-106530	4/1998
JP	11-191319	7/1999
JP	2000-058122	2/2000
JP	2000-182669	6/2000
JP	2001-085056	3/2001
JP	2001-135351	5/2001
JP	2003-017121	1/2003
JP	2004-127943	4/2004
JP	2004-172117	6/2004
JP	2004-172120	6/2004
JP	2004-523073	7/2004
JP	2006-114388	4/2006
JP	2006-351337	12/2006
JP	2007-005242	1/2007
JP	2008-010414	1/2008
JP	2010-533359	10/2010
WO	01/19906	3/2001

OTHER PUBLICATIONS

Chinese Office Action dated Feb. 9, 2018 in corresponding Chinese Application No. 201310132267.1.

* cited by examiner

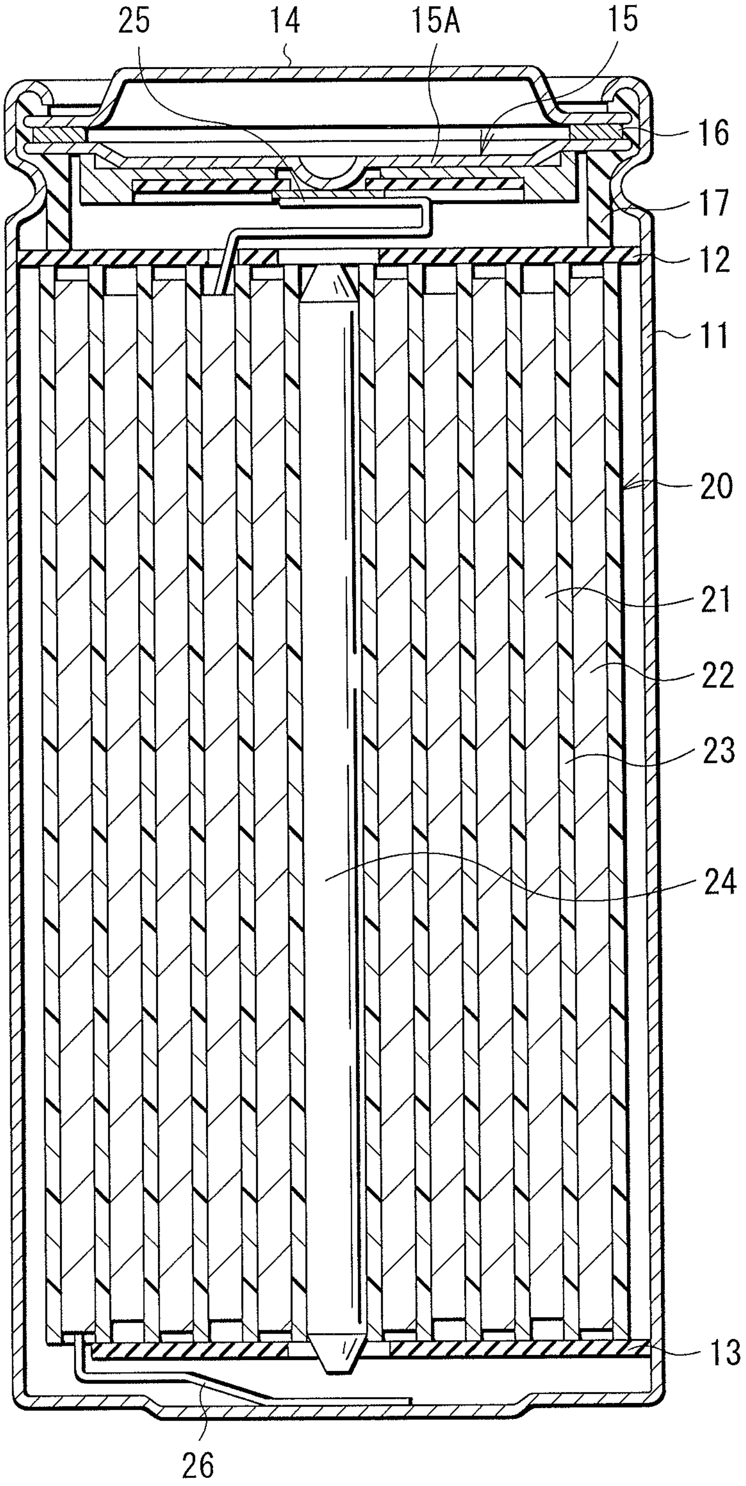


FIG. 1

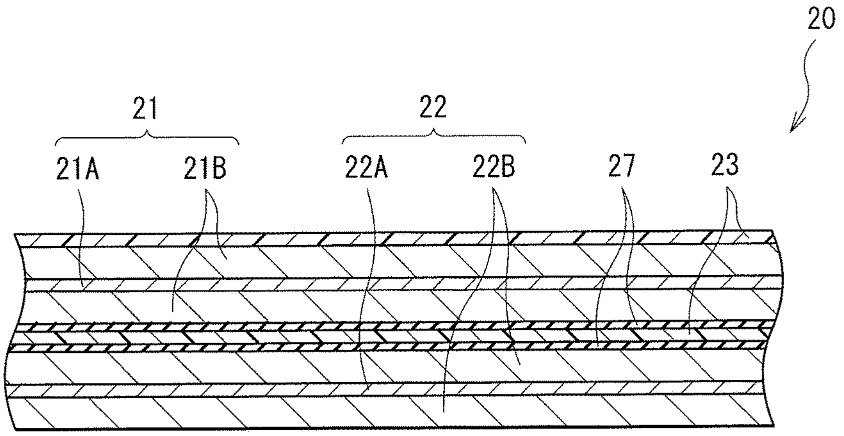


FIG. 2

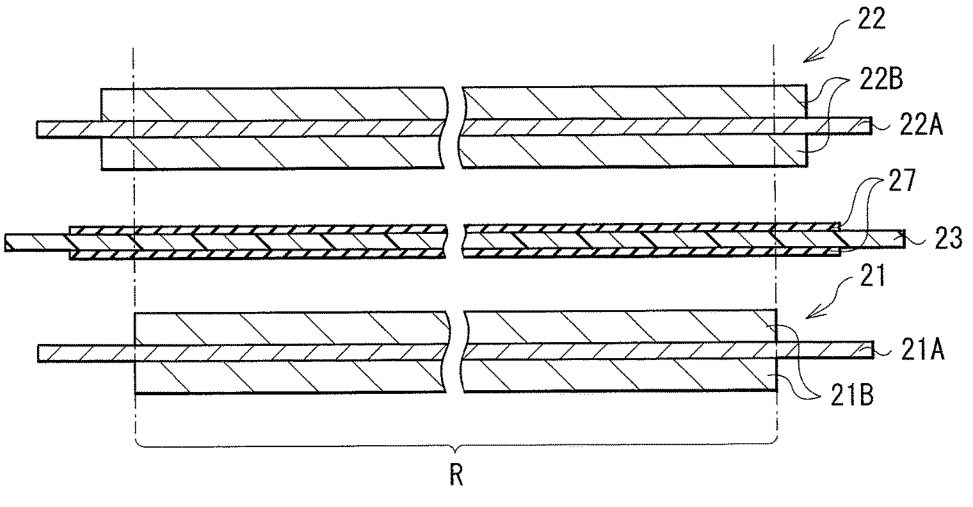


FIG. 3

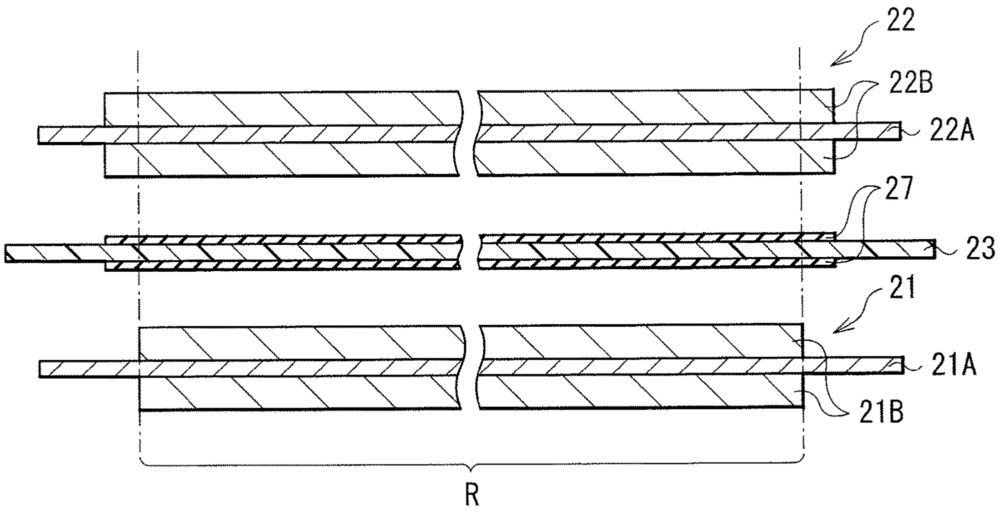


FIG. 4

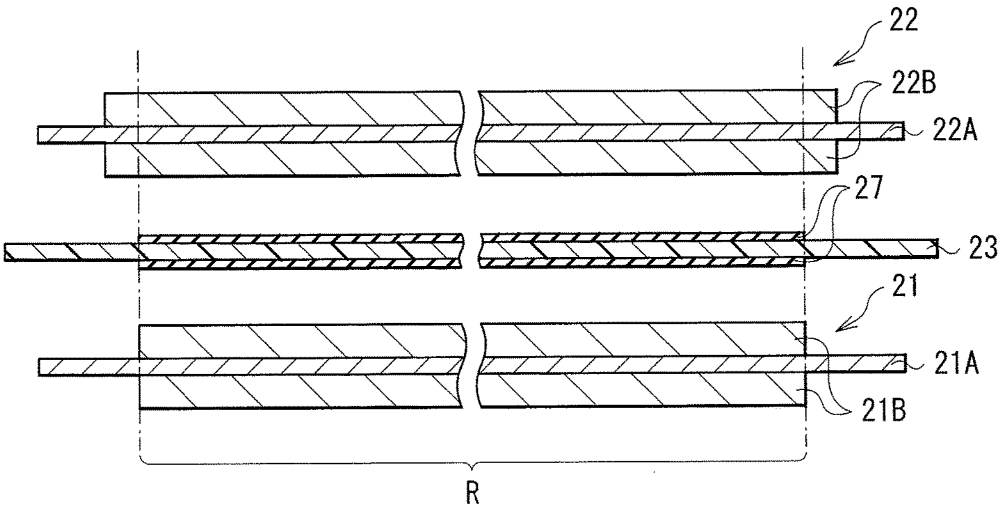


FIG. 5

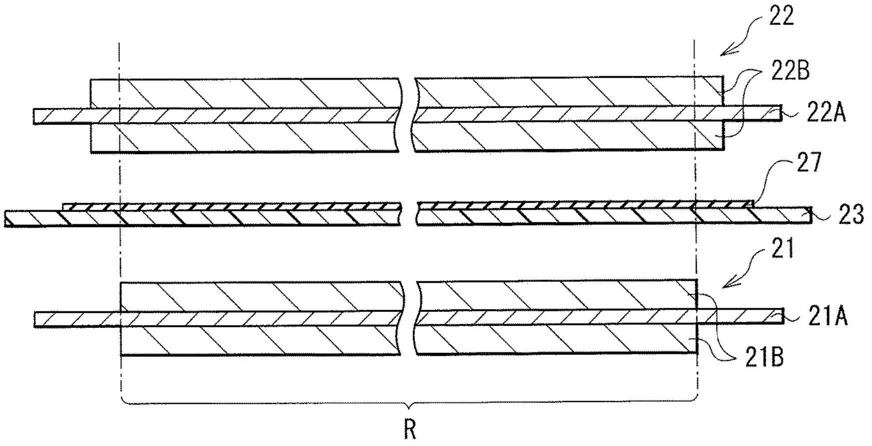


FIG. 6

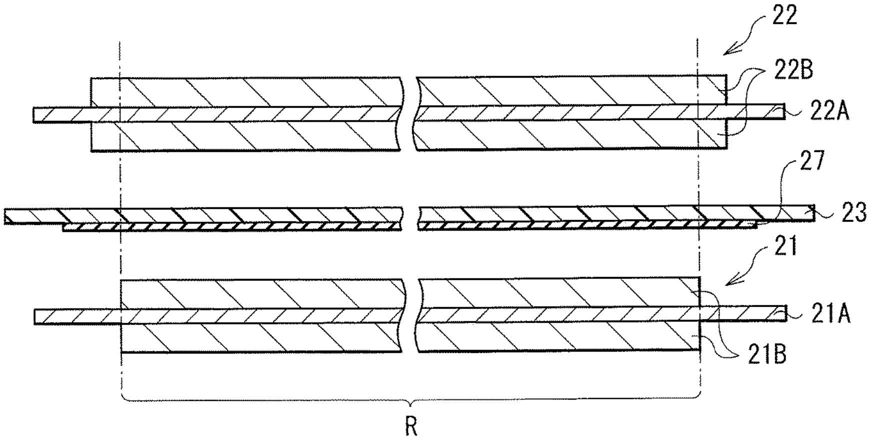


FIG. 7

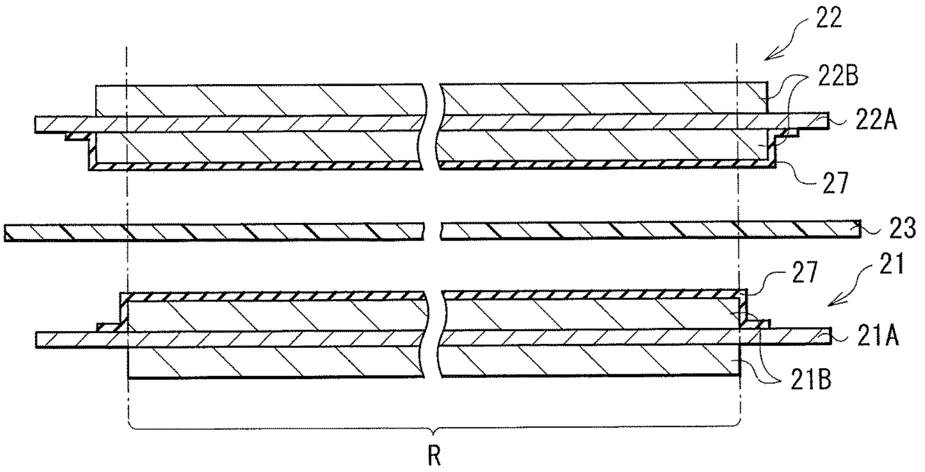


FIG. 8

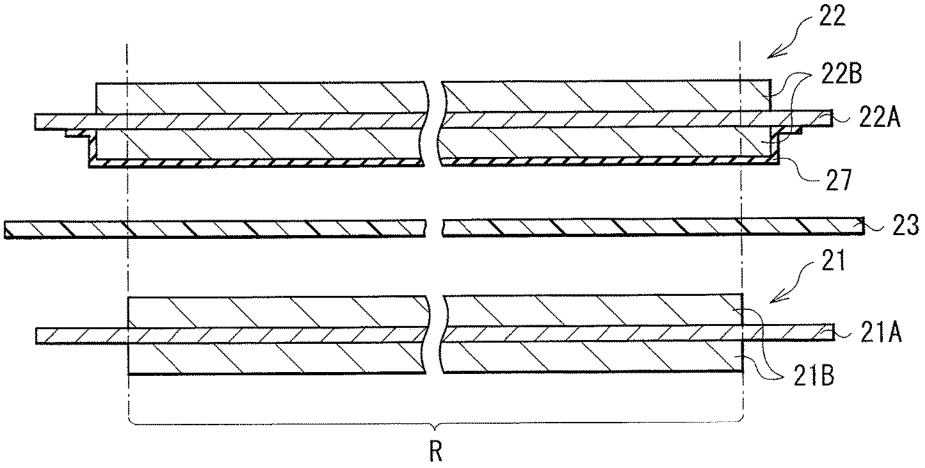


FIG. 9

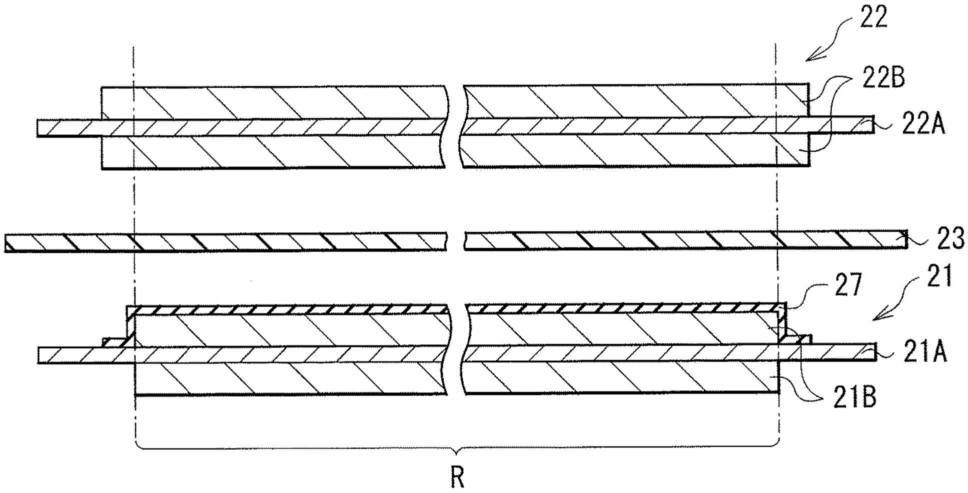


FIG. 10

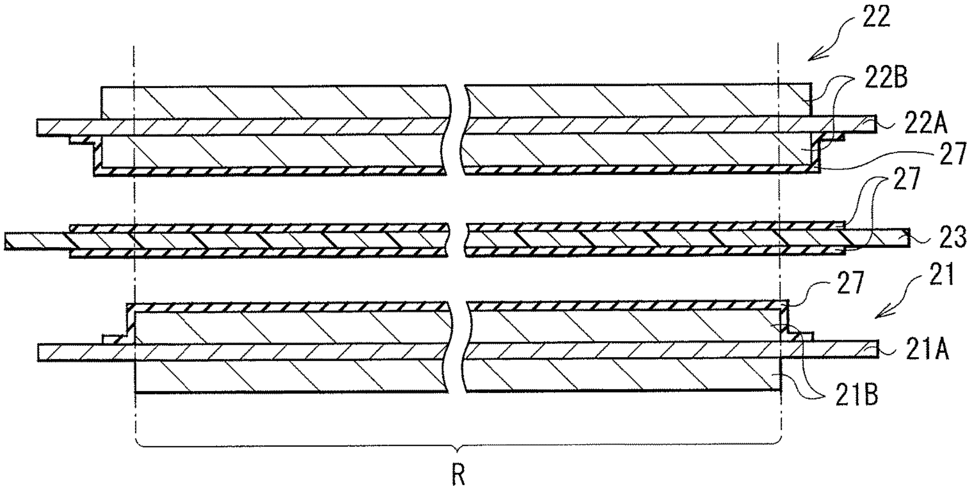


FIG. 11

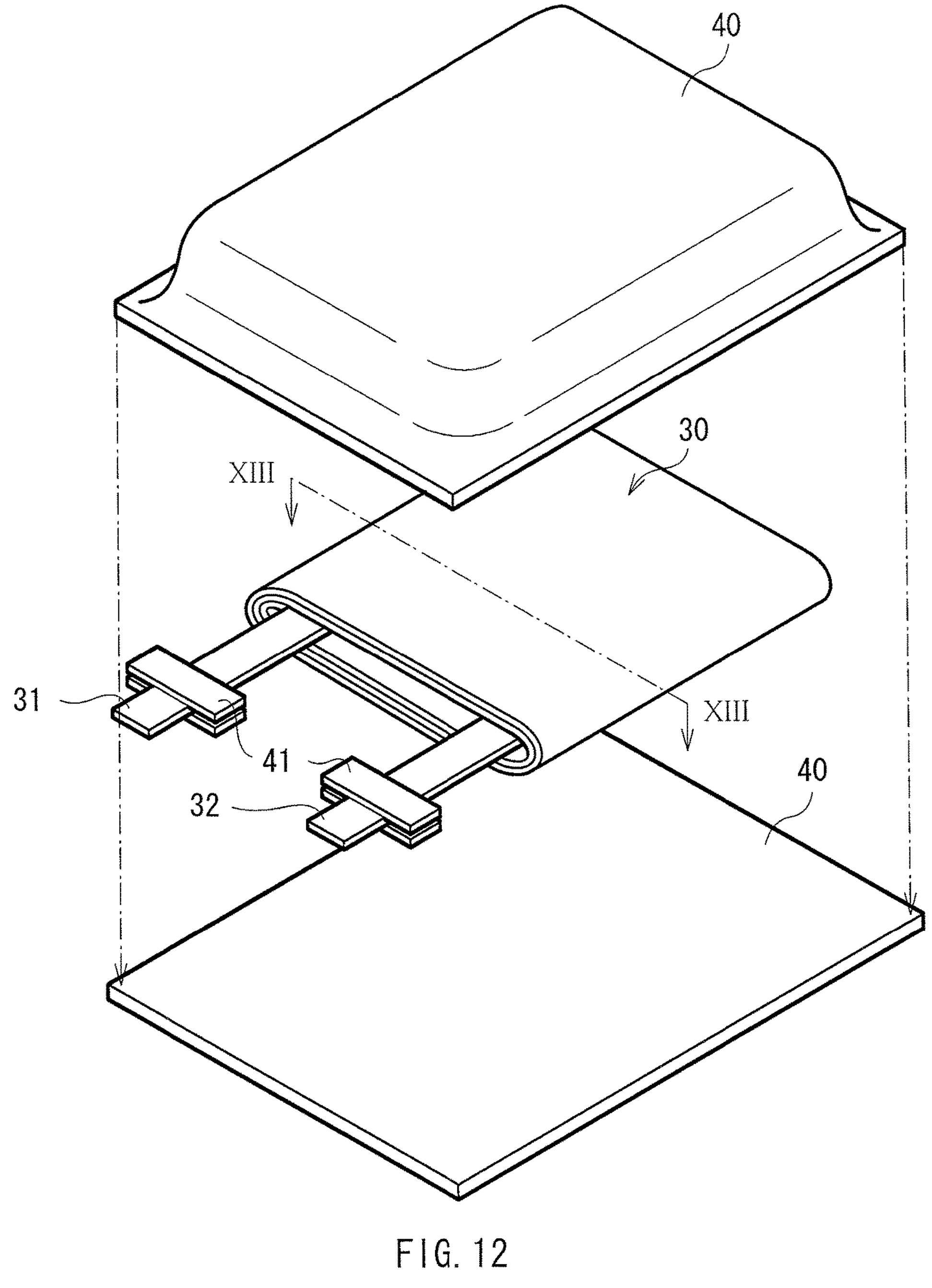


FIG. 12

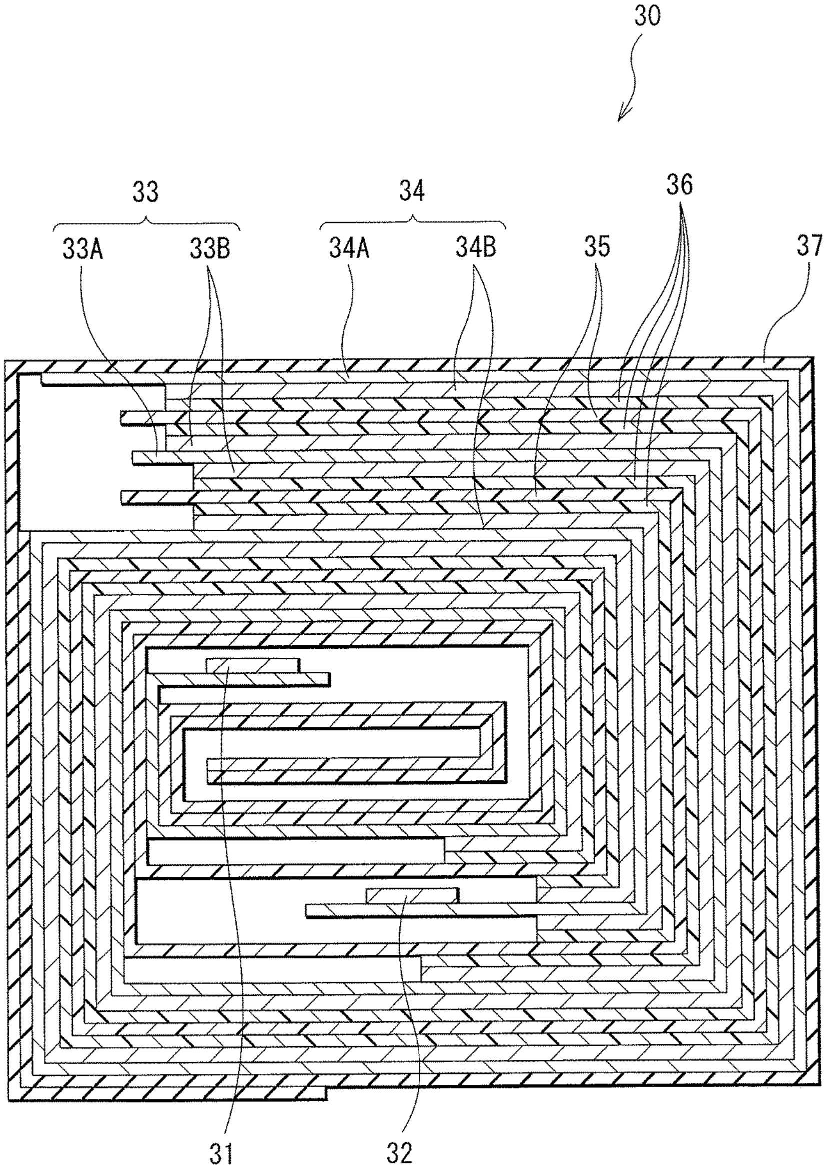


FIG. 13

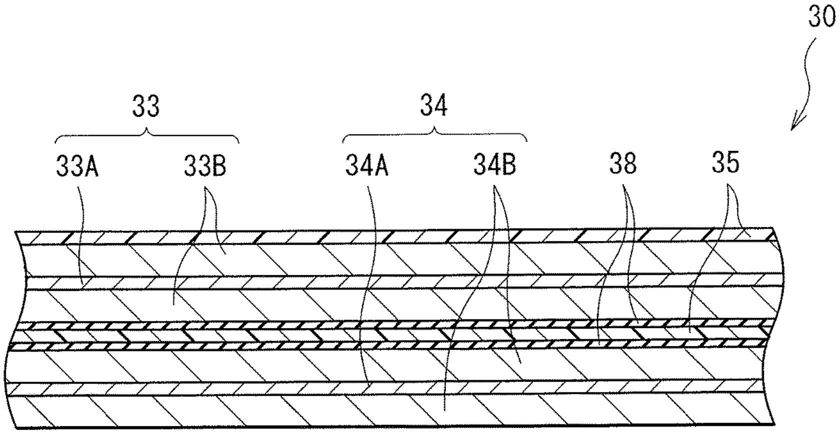


FIG. 14

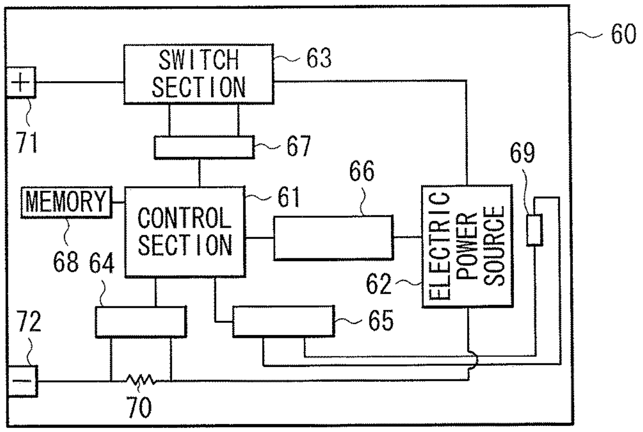

SWITCH SECTION
63
60
+
71
67
69
66
MEMORY
CONTROL SECTION
61
ELECTRIC POWER SOURCE
68
64
62
72
65
−
70

FIG. 15

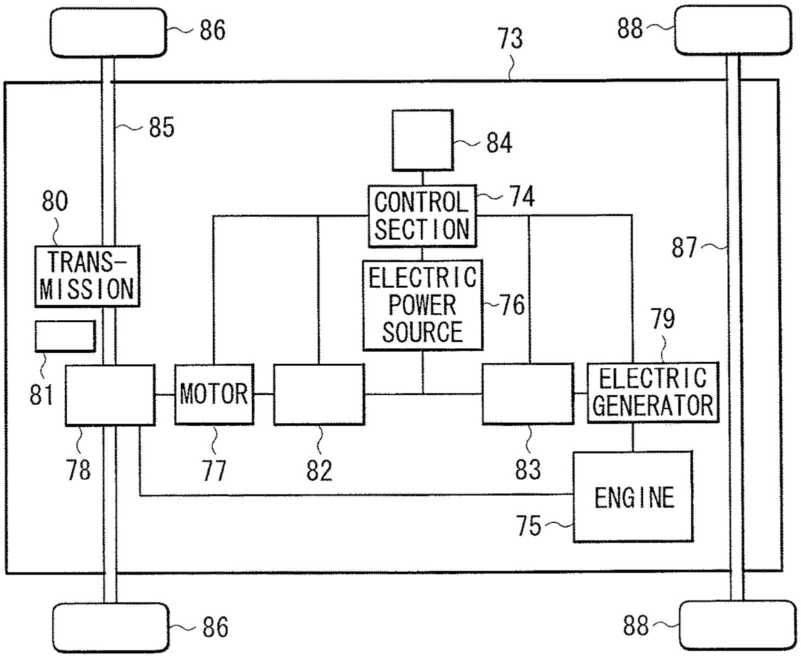

86
73
88
85
84
CONTROL SECTION
74
80
TRANS-MISSION
87
ELECTRIC POWER SOURCE
76
79
81
MOTOR
ELECTRIC GENERATOR
78
77
82
83
ENGINE
75
86
88

FIG. 16

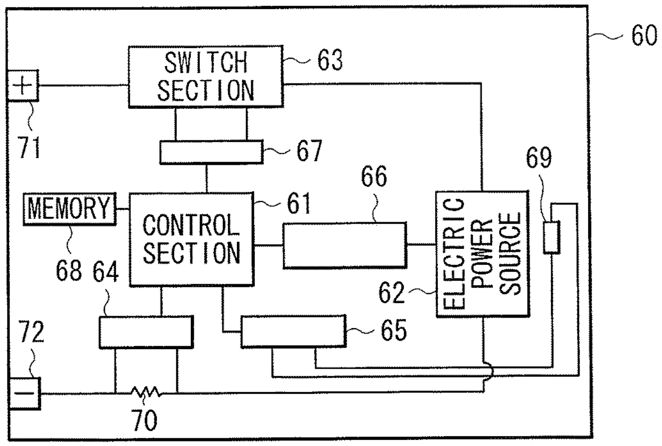

60
SWITCH SECTION
63
+
71
67
69
66
MEMORY
CONTROL SECTION
61
ELECTRIC POWER SOURCE
68
64
62
72
65
−
70

FIG. 17

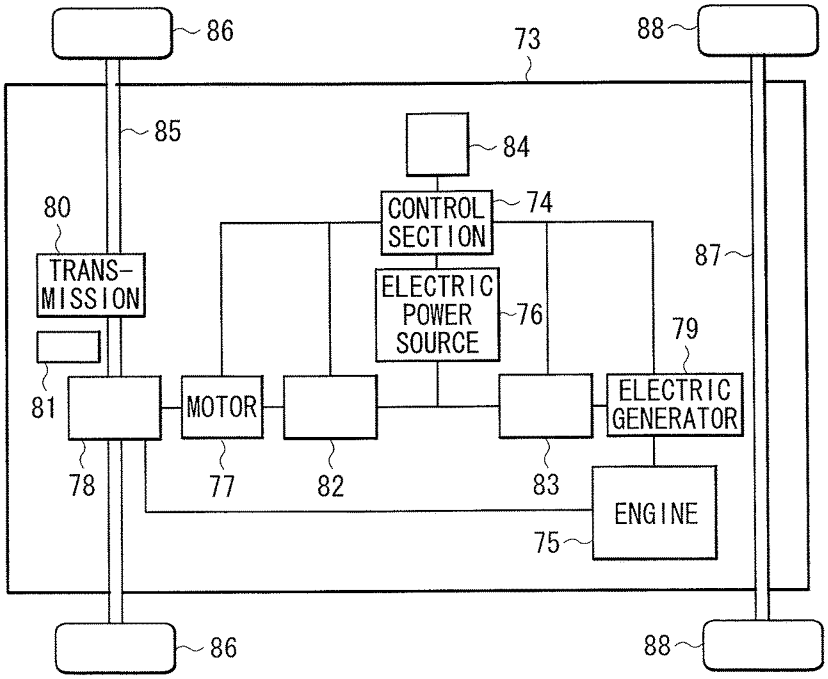

86
73
88
85
84
80
CONTROL SECTION
74
87
TRANS-MISSION
ELECTRIC POWER SOURCE
76
79
81
MOTOR
ELECTRIC GENERATOR
78
77
82
83
ENGINE
75
86
88

FIG. 18

SECONDARY BATTERY, BATTERY PACK, ELECTRIC VEHICLE, ELECTRIC POWER STORAGE SYSTEM, ELECTRIC POWER TOOL, AND ELECTRONIC APPARATUS

CROSS REFERENCES TO RELATED APPLICATIONS

The present application claims priority to Japanese Priority Patent Application JP 2012-092994 filed in the Japan Patent Office on Apr. 16, 2012, the entire content of which is hereby incorporated by reference.

BACKGROUND

The present application relates to a secondary battery including an electrolytic solution together with a cathode and an anode that are opposed to each other with a separator in between, and to a battery pack, an electric vehicle, an electric power storage system, an electric power tool, and an electronic apparatus that use the secondary battery.

In recent years, various electronic apparatuses such as a mobile phone and a personal digital assistant (PDA) have been widely used, and it has been demanded to further reduce the size and the weight of the electronic apparatuses and to achieve their long life. Accordingly, as an electric power source for the electronic apparatuses, a battery, in particular, a small and light-weight secondary battery capable of providing high energy density has been developed. In these days, it has been considered to apply such a secondary battery to various other applications in addition to the foregoing electronic apparatuses. Representative examples of such other applications include a battery pack attachably and detachably mounted on the electronic apparatuses or the like, an electric vehicle such as an electric automobile, an electric power storage system such as a home electric power server, and an electric power tool such as an electric drill.

As the secondary battery, secondary batteries that obtain a battery capacity by utilizing various charge and discharge principles have been proposed. In particular, a secondary battery utilizing insertion and extraction of an electrode reactant is considered promising, since such a secondary battery provides higher energy density than lead batteries, nickel-cadmium batteries, and the like.

The secondary battery includes a cathode, an anode, and an electrolytic solution. The cathode and the anode are opposed to each other with a separator in between, and the electrolytic solution contains a solvent and an electrolyte salt. The configuration of the secondary battery largely affects battery characteristics and the like. Therefore, various studies have been made on the configuration thereof.

Specifically, to suppress battery degradation at the time of high-voltage charging, explosion hazard due to pressure increase inside a battery, and/or the like, a cyclic ester carbonate having one or more carbon-carbon unsaturated bonds is used as an additive of an electrolytic solution (for example, see Japanese Unexamined Patent Application Publication Nos. 2006-114388, 2001-135351, H11-191319, 2000-058122, and 2008-010414, and Japanese Unexamined Patent Application Publication (Translation of PCT Application) No. 2004-523073). This kind of cyclic ester carbonate is used not only for a battery (liquid battery) using an electrolytic solution, but also for a battery not using an electrolytic solution (solid state battery) (for example, see Japanese Unexamined Patent Application Publication No. 2003-017121).

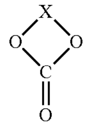
Further, in order to prevent unintentional conduction between a cathode and an anode, particles such as titanium oxide is contained in a separator (for example, see Japanese Unexamined Patent Application Publication Nos. H10-050287, H10-106530, and WO01/019906).

SUMMARY

In recent years, high performance and multi-functions of the electronic apparatuses and the like to which the secondary battery is applied are increasingly developed. Therefore, further improvement of the battery characteristics has been desired.

It is desirable to provide a secondary battery capable of providing superior battery characteristics, a battery pack, an electric vehicle, an electric power storage system, an electric power tool, and an electronic apparatus.

According to an embodiment of the present application, there is provided a secondary battery including: a cathode and an anode that are opposed to each other with a separator in between; and an electrolytic solution. The cathode includes a cathode active material layer on a cathode current collector. The anode includes an anode active material layer on an anode current collector. A heat-resistant layer is provided at least in a region in which the cathode active material layer and the anode active material layer are opposed to each other between the cathode and the anode. The heat-resistant layer includes a material having a higher melting point or higher decomposition temperature than a melting point or decomposition temperature of the separator. The electrolytic solution includes an unsaturated cyclic ester carbonate represented by the following Formula (1),

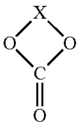


(1)

where X is a divalent group in which m-number of >C═CR1R2 and n-number of >CR3R4 are bonded in any order; each of R1 to R4 is one of a hydrogen group, a halogen group, a monovalent hydrocarbon group, a monovalent halogenated hydrocarbon group, a monovalent oxygen-containing hydrocarbon group, and a monovalent halogenated oxygen-containing hydrocarbon group; any two or more of the R1 to the R4 are allowed to be bonded to one another; and m and n satisfy $m \geq 1$ and $n \geq 0$.

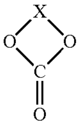
Further, according to an embodiment of the present application, there is provided a battery pack including: a secondary battery; a control section controlling a used state of the secondary battery; and a switch section switching the used state of the secondary battery according to an instruction of the control section. The secondary battery includes a cathode and an anode that are opposed to each other with a separator in between, and an electrolytic solution. The cathode includes a cathode active material layer on a cathode current collector. The anode includes an anode active material layer on an anode current collector. A heat-resistant layer is provided at least in a region in which the cathode active material layer and the anode active material layer are opposed to each other between the cathode and the anode. The heat-resistant layer includes a material having a higher melting point or higher decomposition temperature than a melting point or decomposition temperature of the separator.

The electrolytic solution includes an unsaturated cyclic ester carbonate represented by the following Formula (1),


(1)

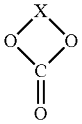
where X is a divalent group in which m-number of >C═CR1R2 and n-number of >CR3R4 are bonded in any order; each of R1 to R4 is one of a hydrogen group, a halogen group, a monovalent hydrocarbon group, a monovalent halogenated hydrocarbon group, a monovalent oxygen-containing hydrocarbon group, and a monovalent halogenated oxygen-containing hydrocarbon group; any two or more of the R1 to the R4 are allowed to be bonded to one another; and m and n satisfy m≥1 and n≥0.

According to an embodiment of the present application, there is provided an electric vehicle including: a secondary battery; a conversion section converting electric power supplied from the secondary battery into drive power; a drive section operating according to the drive power; and a control section controlling a used state of the secondary battery. The secondary battery includes a cathode and an anode that are opposed to each other with a separator in between, and an electrolytic solution. The cathode includes a cathode active material layer on a cathode current collector. The anode includes an anode active material layer on an anode current collector. A heat-resistant layer is provided at least in a region in which the cathode active material layer and the anode active material layer are opposed to each other between the cathode and the anode. The heat-resistant layer includes a material having a higher melting point or higher decomposition temperature than a melting point or decomposition temperature of the separator. The electrolytic solution includes an unsaturated cyclic ester carbonate represented by the following Formula (1),


(1)

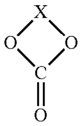
where X is a divalent group in which m-number of >C═CR1R2 and n-number of >CR3R4 are bonded in any order; each of R1 to R4 is one of a hydrogen group, a halogen group, a monovalent hydrocarbon group, a monovalent halogenated hydrocarbon group, a monovalent oxygen-containing hydrocarbon group, and a monovalent halogenated oxygen-containing hydrocarbon group; any two or more of the R1 to the R4 are allowed to be bonded to one another; and m and n satisfy m≥1 and n≥0.

According to an embodiment of the present application, there is provided an electric power storage system including: a secondary battery; one or more electric devices supplied with electric power from the secondary battery; and a control section controlling the supplying of the electric power from the secondary battery to the one or more electric devices. The secondary battery includes a cathode and an anode that are opposed to each other with a separator in between, and an electrolytic solution. The cathode includes a cathode active material layer on a cathode current collector. The anode includes an anode active material layer on an anode current collector. A heat-resistant layer is provided at least in a region in which the cathode active material layer and the anode active material layer are opposed to each other between the cathode and the anode. The heat-resistant layer includes a material having a higher melting point or higher decomposition temperature than a melting point or decomposition temperature of the separator. The electrolytic solution includes an unsaturated cyclic ester carbonate represented by the following Formula (1),


(1)

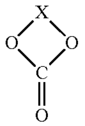
where X is a divalent group in which m-number of >C═CR1R2 and n-number of >CR3R4 are bonded in any order; each of R1 to R4 is one of a hydrogen group, a halogen group, a monovalent hydrocarbon group, a monovalent halogenated hydrocarbon group, a monovalent oxygen-containing hydrocarbon group, and a monovalent halogenated oxygen-containing hydrocarbon group; any two or more of the R1 to the R4 are allowed to be bonded to one another; and m and n satisfy m≥1 and n≥0.

According to an embodiment of the present application, there is provided an electric power tool including: a secondary battery; and a movable section being supplied with electric power from the secondary battery. The secondary battery includes a cathode and an anode that are opposed to each other with a separator in between, and an electrolytic solution. The cathode includes a cathode active material layer on a cathode current collector. The anode includes an anode active material layer on an anode current collector. A heat-resistant layer is provided at least in a region in which the cathode active material layer and the anode active material layer are opposed to each other between the cathode and the anode. The heat-resistant layer includes a material having a higher melting point or higher decomposition temperature than a melting point or decomposition temperature of the separator. The electrolytic solution includes an unsaturated cyclic ester carbonate represented by the following Formula (1),


(1)

where X is a divalent group in which m-number of >C═CR1R2 and n-number of >CR3R4 are bonded in any order; each of R1 to R4 is one of a hydrogen group, a halogen group, a monovalent hydrocarbon group, a monovalent halogenated hydrocarbon group, a monovalent oxygen-containing hydrocarbon group, and a monovalent halogenated oxygen-containing hydrocarbon group; any two or more of the R1 to the R4 are allowed to be bonded to one another; and m and n satisfy m≥1 and n≥0.

According to an embodiment of the present application, there is provided an electronic apparatus including a secondary battery as an electric power supply source. The secondary battery includes a cathode and an anode that are opposed to each other with a separator in between, and an electrolytic solution. The cathode includes a cathode active material layer on a cathode current collector. The anode includes an anode active material layer on an anode current collector. A heat-resistant layer is provided at least in a region in which the cathode active material layer and the anode active material layer are opposed to each other between the cathode and the anode. The heat-resistant layer includes a material having a higher melting point or higher decomposition temperature than a melting point or decomposition temperature of the separator. The electrolytic solution includes an unsaturated cyclic ester carbonate represented by the following Formula (1),



(1)

where X is a divalent group in which m-number of >C═CR1R2 and n-number of >CR3R4 are bonded in any order; each of R1 to R4 is one of a hydrogen group, a halogen group, a monovalent hydrocarbon group, a monovalent halogenated hydrocarbon group, a monovalent oxygen-containing hydrocarbon group, and a monovalent halogenated oxygen-containing hydrocarbon group; any two or more of the R1 to the R4 are allowed to be bonded to one another; and m and n satisfy $m \geq 1$ and $n \geq 0$.

According to the secondary battery according to the embodiment of the present application, the heat-resistant layer is included at least in the region in which the cathode active material layer and the anode active material layer are opposed to each other between the cathode and the anode, the heat-resistant layer includes the material having the higher melting point or the higher decomposition temperature than the melting point or the decomposition temperature of the separator, and the electrolytic solution includes the unsaturated cyclic ester carbonate. Therefore, superior battery characteristics are obtainable. Further, according to the battery pack, the electric vehicle, the electric power storage system, the electric power tool, and the electronic apparatus according to the embodiments of the present application, similar effects are obtainable.

It is to be understood that both the foregoing general description and the following detailed description are exemplary, and are intended to provide further explanation of the application as claimed.

Additional features and advantages are described herein, and will be apparent from the following Detailed Description and the figures.

BRIEF DESCRIPTION OF THE FIGURES

The accompanying drawings are included to provide a further understanding of the disclosure, and are incorporated in and constitute a part of this specification. The drawings illustrate embodiments and, together with the specification, serve to explain the principles of the application.

FIG. **1** is a cross-sectional view illustrating a configuration of a secondary battery (cylindrical type) according to an embodiment of the present application.

FIG. **2** is a cross-sectional view illustrating an enlarged part of a spirally wound electrode body illustrated in FIG. **1**.

FIG. **3** is another cross-sectional view illustrating an enlarged part of the spirally wound electrode body illustrated in FIG. **1**.

FIG. **4** is a cross-sectional view illustrating a first modification of a configuration of the spirally wound electrode body.

FIG. **5** is a cross-sectional view illustrating a second modification of the configuration of the spirally wound electrode body.

FIG. **6** is a cross-sectional view illustrating a third modification of the configuration of the spirally wound electrode body.

FIG. **7** is a cross-sectional view illustrating a fourth modification of the configuration of the spirally wound electrode body.

FIG. **8** is a cross-sectional view illustrating a fifth modification of the configuration of the spirally wound electrode body.

FIG. **9** is a cross-sectional view illustrating a sixth modification of the configuration of the spirally wound electrode body.

FIG. **10** is a cross-sectional view illustrating a seventh modification of the configuration of the spirally wound electrode body.

FIG. **11** is a cross-sectional view illustrating an eighth modification of the configuration of the spirally wound electrode body.

FIG. **12** is a perspective view illustrating a configuration of another secondary battery (laminated film type) according to the embodiment of the present application.

FIG. **13** is a cross-sectional view taken along a line XIII—XIII of a spirally wound electrode body illustrated in FIG. **12**.

FIG. **14** is a cross-sectional view illustrating an enlarged part of a spirally wound electrode body illustrated in FIG. **13**.

FIG. **15** is a block diagram illustrating a configuration of an application example (battery pack) of the secondary battery.

FIG. **16** is a block diagram illustrating a configuration of an application example (electric vehicle) of the secondary battery.

FIG. **17** is a block diagram illustrating a configuration of an application example (electric power storage system) of the secondary battery.

FIG. **18** is a block diagram illustrating a configuration of an application example (electric power tool) of the secondary battery.

DETAILED DESCRIPTION

An embodiment of the present application will be described in detail with reference to the drawings. The description will be given in the following order.

1. Secondary Battery
1-1. Cylindrical Type
1-2. Modifications
1-3. Laminated Film Type
2. Applications of Secondary Battery
2-1. Battery Pack
2-2. Electric Vehicle
2-3. Electric Power Storage System
2-4. Electric Power Tool

[1. Secondary Battery]

[1-1. Cylindrical Type]

FIG. **1** to FIG. **3** illustrate cross-sectional configurations of a secondary battery according to an embodiment of the present application. FIG. **2** and FIG. **3** illustrate enlarged part of a spirally wound electrode body **20** illustrated in FIG. **1**. FIG. **2** illustrates part in the course of the spirally winding direction of the spirally wound electrode body **20**. FIG. **3** schematically illustrates a whole configuration of partial components (a cathode **21**, an anode **22**, and a separator **23**) of the spirally wound electrode body **20**

[Whole Configuration of Secondary Battery]

The secondary battery described here is a lithium ion secondary battery in which the capacity of the anode **22** is obtained by insertion and extraction of Li (lithium ions) as an electrode reactant.

The secondary battery is, for example, as illustrated in FIG. **1**, a so-called cylindrical-type secondary battery. The secondary battery contains the spirally wound electrode body **20** and a pair of insulating plates **12** and **13** inside a battery can **11** in the shape of a substantially hollow cylinder. In the spirally wound electrode body **20**, for example, the cathode **21** and the anode **22** are opposed to each other (layered) with a separator **23** in between, and are subsequently spirally wound.

The battery can **11** has a hollow structure in which one end of the battery can **11** is closed and the other end of the battery can **11** is opened. The battery can **11** may be made of, for example, iron, aluminum, an alloy thereof, or the like. It is to be noted that the surface of the battery can **11** may be plated with nickel or the like. The pair of insulating plates **12** and **13** is arranged to sandwich the spirally wound electrode body **20** in between, and to extend perpendicularly to the spirally wound periphery surface.

At the open end of the battery can **11**, a battery cover **14**, a safety valve mechanism **15**, and a positive temperature coefficient device (PTC device) **16** are attached by being swaged with a gasket **17**. Thereby, the battery can **11** is hermetically sealed. The battery cover **14** may be made of, for example, a material similar to that of the battery can **11**. The safety valve mechanism **15** and the PTC device **16** are provided inside the battery cover **14**. The safety valve mechanism **15** is electrically connected to the battery cover **14** through the PTC device **16**. In the safety valve mechanism **15**, in the case where the internal pressure becomes a certain level or more by internal short circuit, external heating, or the like, a disk plate **15**A inverts to cut electric connection between the battery cover **14** and the spirally wound electrode body **20**. The PTC device **16** prevents abnormal heat generation resulting from a large current. As temperature rises, resistance of the PTC device **16** is increased accordingly. The gasket **17** is made of, for example, an insulating material. The surface of the gasket **17** may be coated with asphalt.

In the center of the spirally wound electrode body **20**, for example, a center pin **24** is inserted. However, the center pin **24** is not necessarily included therein. For example, a cathode lead **25** made of a conductive material such as aluminum is connected to the cathode **21**. For example, an anode lead **26** made of a conductive material such as nickel is connected to the anode **22**. The cathode lead **25** is attached to the safety valve mechanism **15** by welding or the like, and is electrically connected to the battery cover **14**. The anode lead **26** is attached to the battery can **11** by welding or the like, and is electrically connected to the battery can **11**.

[Cathode]

The cathode **21** has, for example, as illustrated in FIG. **2**, a cathode active material layer **21**B on a single surface or both surfaces of a cathode current collector **21**A. The cathode current collector **21**A is made of, for example, a conductive material such as aluminum, nickel, and stainless steel.

The cathode active material layer **21**B contains, as cathode active materials, one or more of cathode materials capable of inserting and extracting lithium ions. The cathode active material layer **21**B may further contain other materials such as a cathode binder and a cathode electric conductor as necessary.

The cathode material is preferably a lithium-containing compound, since high energy density is thereby obtained. Examples of the lithium-containing compound include a lithium-transition-metal composite oxide and a lithium-transition-metal-phosphate compound. The lithium-transition-metal composite oxide is an oxide containing Li and one or more transition metal elements as constituent elements. The lithium-transition-metal-phosphate compound is a phosphate compound containing Li and one or more transition metal elements as constituent elements. In particular, it is preferable that the transition metal element be one or more of Co, Ni, Mn, Fe, and the like, since a higher voltage is obtained thereby. The chemical formula thereof is expressed by, for example, Li_xM1O_2 or Li_yM2PO_4. In the formulas, M1 and M2 represent one or more transition metal elements. Values of x and y vary according to the charge and discharge state, and are generally in the range of $0.05 \le x \le 1.10$ and $0.05 \le y \le 1.10$.

Examples of the lithium-transition-metal composite oxide include $LiCoO_2$, $LiNiO_2$, and a lithium-nickel-based composite oxide represented by the following Formula (20). Examples of the lithium-transition-metal-phosphate compound include $LiFePO_4$ and $LiFe_{1-u}Mn_uPO_4$ (u<1), since thereby, a high battery capacity is obtained and superior cycle characteristics are obtained.

$$LiNi_{1-z}M_zO_2 \quad (20)$$

In Formula (20), M is one or more of Co, Mn, Fe, Al, V, Sn, Mg, Ti, Sr, Ca, Zr, Mo, Tc, Ru, Ta, W, Re, Yb, Cu, Zn, Ba, B, Cr, Si, Ga, P, Sb, and Nb. z satisfies $0.005<z<0.5$.

In addition thereto, the cathode material may be, for example, an oxide, a disulfide, a chalcogenide, a conductive polymer, or the like. Examples of the oxide include titanium oxide, vanadium oxide, and manganese dioxide. Examples of the disulfide include titanium disulfide and molybdenum sulfide. Examples of the chalcogenide include niobium selenide. Examples of the conductive polymer include sulfur, polyaniline, and polythiophene. However, the cathode material is not limited to the foregoing materials.

Examples of the cathode binder include one or more of synthetic rubbers, polymer materials, and the like. Examples of the synthetic rubber include a styrene-butadiene-based rubber, a fluorine-based rubber, and ethylene propylene diene. Examples of the polymer material include polyvinylidene fluoride and polyimide.

Examples of the cathode electric conductor include one or more of carbon materials and the like. Examples of the carbon materials include graphite, carbon black, acetylene black, and Ketjen black. The cathode electric conductor may be a metal material, a conductive polymer, or the like as long as the material has electric conductivity.

[Anode]

The anode **22** has, for example, as illustrated in FIG. **2**, an anode active material layer **22**B on a single surface or both surfaces of an anode current collector **22**A.

The anode current collector **22**A is made of, for example, a conductive material such as copper, nickel, and stainless steel. The surface of the anode current collector **22**A is preferably roughened. Thereby, due to a so-called anchor effect, adhesion characteristics of the anode active material layer **22**B with respect to the anode current collector **22**A are improved. In this case, it is enough that the surface of the anode current collector **22**A in a region opposed to the anode active material layer **22**B is roughened at minimum. Examples of roughening methods include a method of forming fine particles by utilizing electrolytic treatment. The electrolytic treatment is a method of providing concavity and convexity by forming fine particles on the surface of the anode current collector **22**A by using an electrolytic method in an electrolytic bath. A copper foil fabricated by an electrolytic method is generally called "electrolytic copper foil."

The anode active material layer **22**B contains one or more of anode materials capable of inserting and extracting lithium ions as anode active materials, and may also contain other materials such as an anode binder and an anode electric conductor as necessary. Details of the anode binder and the anode electric conductor are, for example, similar to those of the cathode binder and the cathode electric conductor, respectively. However, the chargeable capacity of the anode material is preferably larger than the discharge capacity of the cathode **21** in order to prevent lithium metal from being unintentionally precipitated on the anode **22** in the middle of charge.

The anode material is, for example, a carbon material. In the carbon material, its crystal structure change at the time of insertion and extraction of lithium ions is extremely small. Therefore, the carbon material provides high energy density and superior cycle characteristics. Further, the carbon material functions as an anode electric conductor as well. Examples of the carbon material include graphitizable carbon, non-graphitizable carbon in which the spacing of (002) plane is equal to or greater than 0.37 nm, and graphite in which the spacing of (002) plane is equal to or smaller than 0.34 nm. More specifically, examples of the carbon material include pyrolytic carbons, cokes, glassy carbon fiber, an organic polymer compound fired body, activated carbon, and carbon blacks. Of the foregoing, examples of the cokes include pitch coke, needle coke, and petroleum coke. The organic polymer compound fired body is obtained by firing (carbonizing) a polymer compound such as a phenol resin and a furan resin at appropriate temperature. In addition thereto, the carbon material may be low crystalline carbon or amorphous carbon heat-treated at temperature of about 1000 deg C. or less. It is to be noted that the shape of the carbon material may be any of a fibrous shape, a spherical shape, a granular shape, and a scale-like shape.

Further, the anode material is, for example, a material (metal-based material) containing one or more of metal elements and metalloid elements as constituent elements, since higher energy density is thereby obtained. Such a metal-based material may be a simple substance, an alloy, or a compound, may be two or more thereof, or may have one or more phases thereof in part or all thereof. "Alloy" includes a material containing one or more metal elements and one or more metalloid elements, in addition to a material configured of two or more metal elements. Further, the "alloy" may contain a nonmetallic element. Examples of the structure thereof include a solid solution, a eutectic crystal (eutectic mixture), an intermetallic compound, and a structure in which two or more thereof coexist.

Examples of the foregoing metal elements and the foregoing metalloid elements include one or more of metal elements and metalloid elements capable of forming an alloy with Li. Specific examples thereof include Mg, B, Al, Ga, In, Si, Ge, Sn, Pb, Bi, Cd, Ag, Zn, Hf, Zr, Y, Pd, and Pt. In particular, Si, Sn, or both are preferable. Si and Sn have a superior ability of inserting and extracting lithium ions, and therefore, provide high energy density.

A material containing Si, Sn, or both as constituent elements may be a simple substance, an alloy, or a compound of Si or Sn, may be two or more thereof, or may have one or more phases thereof in part or all thereof. The simple substance merely refers to a general simple substance (a small amount of impurity may be therein contained), and does not necessarily refer to a purity 100% simple substance.

The alloys of Si contain one or more of elements such as Sn, Ni, Cu, Fe, Co, Mn, Zn, In, Ag, Ti, Ge, Bi, Sb, and Cr as constituent elements other than Si. The compounds of Si contain one or more of C, O, and the like as constituent elements other than Si. For example, the compounds of Si may contain one or more of the elements described for the alloys of Si as constituent elements other than Si.

Examples of the alloys of Si and the compounds of Si include SiB_4, SiB_6, Mg_2Si, Ni_2Si, $TiSi_2$, $MoSi_2$, $CoSi_2$, $NiSi_2$, $CaSi_2$, $CrSi_2$, Cu_5Si, $FeSi_2$, $MnSi_2$, $NbSi_2$, $TaSi_2$, VSi_2, WSi_2, $ZnSi_2$, SiC, Si_3N_4, Si_2N_2O, SiO_v ($0<v\leq2$), and LiSiO. v in SiO_v may be in the range of $0.2<v<1.4$.

The alloys of Sn contain, for example, one or more of elements such as Si, Ni, Cu, Fe, Co, Mn, Zn, In, Ag, Ti, Ge, Bi, Sb, and Cr as constituent elements other than Sn. The compounds of Sn contain, for example, one or more of elements such as C and O as constituent elements other than Sn. It is to be noted that the compounds of Sn may contain, for example, one or more of elements described for the alloys of Sn as constituent elements other than Sn. Examples of the alloys of Sn and the compounds of Sn include SnO_w ($0<w\leq2$), $SnSiO_3$, LiSnO, and Mg_2Sn.

Further, as a material containing Sn, for example, a material containing a second constituent element and a third constituent element in addition to Sn as a first constituent element is preferable. Examples of the second constituent element include one or more of elements such as Co, Fe, Mg, Ti, V, Cr, Mn, Ni, Cu, Zn, Ga, Zr, Nb, Mo, Ag, In, Ce, Hf, Ta, W, Bi, and Si. Examples of the third constituent element include one or more of B, C, Al, P, and the like. In the case where the second constituent element and the third constituent element are contained, a high battery capacity, superior cycle characteristics, and the like are obtained.

In particular, a material containing Sn, Co, and C as constituent elements (SnCoC-containing material) is preferable. The composition of the SnCoC-containing material is, for example, as follows. That is, the C content is from 9.9 mass % to 29.7 mass % both inclusive, and the ratio of Sn and Co contents (Co/(Sn+Co)) is from 20 mass % to 70 mass % both inclusive, since high energy density is obtained in such a composition range.

It is preferable that the SnCoC-containing material have a phase containing Sn, Co, and C. Such a phase is preferably low-crystalline or amorphous. The phase is a reaction phase capable of reacting with Li. Due to existence of the reaction phase, superior characteristics are obtained. The half bandwidth of the diffraction peak obtained by X-ray diffraction of the phase is preferably equal to or greater than 1 deg based on diffraction angle of 2θ in the case where CuKα ray is used as a specific X ray, and the insertion rate is 1 deg/min. Thereby, lithium ions are more smoothly inserted and extracted, and reactivity with the electrolytic solution is decreased. It is to be noted that, in some cases, the SnCoC-containing material includes a phase containing a simple substance or part of the respective constituent elements in addition to the low-crystalline phase or the amorphous phase.

Whether or not the diffraction peak obtained by the X-ray diffraction corresponds to the reaction phase capable of reacting with Li is allowed to be easily determined by comparison between X-ray diffraction charts before and after electrochemical reaction with Li. For example, if the position of the diffraction peak after electrochemical reaction with Li is changed from the position of the diffraction peak before the electrochemical reaction with Li, the obtained diffraction peak corresponds to the reaction phase capable of reacting with Li. In this case, for example, the diffraction peak of the low crystalline reaction phase or the amorphous reaction phase is seen in the range of 2θ=from 20 deg to 50 deg both inclusive. Such a reaction phase has, for example, the foregoing respective constituent elements, and the low crystalline or amorphous structure thereof possibly results from existence of C mainly.

In the SnCoC-containing material, part or all of C as a constituent element are preferably bonded to a metal element or a metalloid element as other constituent element, since cohesion or crystallization of Sn and/or the like is suppressed thereby. The bonding state of elements is allowed to be checked by, for example, X-ray photoelectron spectroscopy (XPS). In a commercially available device, for example, as a soft X ray, Al—Kα ray, Mg—Kα ray, or the like is used. In the case where part or all of C are bonded to a metal element, a metalloid element, or the like, the peak of a synthetic wave of 1s orbit of C (C1s) is shown in a region lower than 284.5 eV. In the device, energy calibration is made so that the peak of 4f orbit of Au atom (Au4f) is obtained in 84.0 eV. At this time, in general, since surface contamination carbon exists on the material surface, the peak of C1s of the surface contamination carbon is regarded as 284.8 eV, which is used as the energy standard. In XPS measurement, the waveform of the peak of C1s is obtained as a form including the peak of the surface contamination carbon and the peak of carbon in the SnCoC-containing material. Therefore, for example, analysis is made by using commercially available software to isolate both peaks from each other. In the waveform analysis, the position of the main peak existing on the lowest bound energy side is the energy standard (284.8 eV).

It is to be noted that the SnCoC-containing material is not limited to the material (SnCoC) configured of only Sn, Co, and C as constituent elements. That is, the SnCoC-containing material may further contain, for example, one or more of Si, Fe, Ni, Cr, In, Nb, Ge, Ti, Mo, Al, P, Ga, Bi, and the like as constituent elements as necessary.

In addition to the SnCoC-containing material, a material containing Sn, Co, Fe, and C as constituent elements (SnCoFeC-containing material) is also preferable. The composition of the SnCoFeC-containing material may be arbitrarily set. For example, the composition in which the Fe content is set small is as follows. That is, the C content is from 9.9 mass % to 29.7 mass % both inclusive, the Fe content is from 0.3 mass % to 5.9 mass % both inclusive, and the ratio of contents of Sn and Co (Co/(Sn+Co)) is from 30 mass % to 70 mass % both inclusive. Further, the composition in which the Fe content is set large is as follows. That is, the C content is from 11.9 mass % to 29.7 mass % both inclusive, the ratio of contents of Sn, Co, and Fe ((Co+Fe)/(Sn+Co+Fe)) is from 26.4 mass % to 48.5 mass % both inclusive, and the ratio of contents of Co and Fe (Co/(Co+Fe)) is from 9.9 mass % to 79.5 mass % both inclusive. In such a composition range, high energy density is obtained. The physical properties (such as half bandwidth) of the SnCoFeC-containing material are similar to those of the foregoing SnCoC-containing material.

In addition thereto, the anode material may be, for example, a metal oxide, a polymer compound, or the like. Examples of the metal oxide include iron oxide, ruthenium oxide, and molybdenum oxide. Examples of the polymer compound include polyacetylene, polyaniline, and polypyrrole.

The anode active material layer **22**B is formed by, for example, a coating method, a vapor-phase deposition method, a liquid-phase deposition method, a spraying method, a firing method (sintering method), or a combination of two or more of these methods. The coating method is a method in which, for example, after a particulate (powder) anode active material is mixed with an anode binder and/or the like, the mixture is dispersed in a solvent such as an organic solvent, and the anode current collector **22**A is coated with the resultant. Examples of the vapor-phase deposition method include a physical deposition method and a chemical deposition method. More specifically, examples thereof include a vacuum evaporation method, a sputtering method, an ion plating method, a laser ablation method, a thermal chemical vapor deposition method, a chemical vapor deposition (CVD) method, and a plasma chemical vapor deposition method. Examples of the liquid-phase deposition method include an electrolytic plating method and an electroless plating method. The spraying method is a method in which an anode active material in a fused state or a semi-fused state is sprayed to the anode current collector **22**A. The firing method is, for example, a method in which after the anode current collector **22**A is coated by using a coating method, heat treatment is performed at temperature higher than the melting point of the anode binder and/or the like. Examples of the firing method include a publicly-known technique such as an atmosphere firing method, a reactive firing method, and a hot press firing method.

In the secondary battery, as described above, in order to prevent lithium metal from being unintentionally precipitated on the anode **22** in the middle of charge, the electrochemical equivalent of the anode material capable of inserting and extracting lithium ions is preferably larger than the electrochemical equivalent of the cathode. Further, in the case where the open circuit voltage (that is, a battery voltage) at the time of completely-charged state is equal to or greater than 4.25 V, the extraction amount of lithium ions per unit mass is larger than that in the case where the open circuit voltage is 4.2 V even if the same cathode active material is used. Therefore, amounts of the cathode active material and the anode active material are adjusted accordingly. Thereby, high energy density is obtainable.

For example, as illustrated in FIG. **3**, the cathode active material layer **21**B is provided in part of surfaces of the cathode current collector **21**A, and the anode active material layer **22**B is provided in part of surfaces of the anode current collector **22**A as the cathode active material layer **21**B is.

In this case, the cathode active material layer **21**B is provided, for example, in the central region in the longitudinal direction of the cathode current collector **21**A. Therefore, the central region of the cathode current collector **21**A is covered with the cathode active material layer **21**B, and edge regions thereof on the inner side and on the outer side of the spirally wound body are not covered with the cathode active material layer **21**B and are exposed. Further, the anode active material layer **22**B is provided, for example, in the central region in the longitudinal direction of the anode current collector **22**A. Therefore, the central region of the anode current collector **22**A is covered with the anode active material layer **22**B, and edge regions thereof on the inner side and on the outer side of the spirally wound body are not covered with the anode active material layer **22**B and are exposed.

However, the formation range of the anode active material layer **22**B in the longitudinal direction of the anode current collector **22**A is extended toward both the inner side and the outer side of the spirally wound body, the formation range of the anode active material layer **22**B being beyond the formation range of the cathode active material layer **21**B in the longitudinal direction of the cathode current collector **21**A. Thereby, the anode active material layer **22**B includes a region (opposed region R) opposed to the cathode active material layer **21**B and a region (non-opposed region) not opposed to the cathode active material layer **21**B. One reason for this is that, by maximizing the opposed region R in which the cathode active material layer **21**B and the anode active material layer **22**B are opposed to each other, a region where charge and discharge are allowed to be performed is secured. Another reason for this is that lithium metal is thereby prevented from being unintentionally precipitated on the surface of anode current collector **22**A. Of the anode active material layer **22**B, a portion located in the opposed region R is involved in charge and discharge, while a portion located in the non-opposed region is less likely to be involved in charge and discharge.

[Separator]

The separator **23** separates the cathode **21** from the anode **22**, and passes lithium ions while preventing current short circuit resulting from contact of both electrodes. The separator **23** is, for example, a porous film made of a synthetic resin, ceramics, or the like. The separator **23** may be a laminated film in which two or more types of porous films are laminated. Examples of the synthetic resin include polytetrafluoroethylene, polypropylene, and polyolefin such as polyethylene. As melting points or decomposition temperature of the representative synthetic resins, the melting point or the decomposition temperature of polyethylene is about 130 deg C., and the melting point or the decomposition temperature of polypropylene is about 170 deg C.

In particular, the separator **23** may include, for example, the foregoing porous film (base material layer) and a polymer compound layer provided on one surface or both surfaces of the base material layer. Thereby, adhesion characteristics of the separator **23** with respect to the cathode **21** and the anode **22** are improved, and therefore, skewness of the spirally wound electrode body **20** is suppressed. Thereby, a decomposition reaction of the electrolytic solution is suppressed, and liquid leakage of the electrolytic solution with which the base material layer is impregnated is suppressed. Accordingly, even if charge and discharge are repeated, the resistance of the secondary battery is less likely to be increased, and battery swollenness is suppressed.

The polymer compound layer contains, for example, a polymer material such as polyvinylidene fluoride, since such a polymer material has a superior physical strength and is electrochemically stable. However, the polymer material may be a material other than polyvinylidene fluoride. The polymer compound layer is formed as follows, for example. That is, after a solution in which the polymer material is dissolved is prepared, the base material layer is coated with the solution, and the resultant is subsequently dried. Alternatively, the base material layer may be soaked in the solution and may be subsequently dried.

[Heat-Resistant Layer]

A heat-resistant layer **27** is provided at least in the opposed region (the opposed region R illustrated in FIG. **3**) in which the cathode active material layer **21**B and the anode active material layer **22**B are opposed to each other between the cathode **21** and the anode **22**. In this case, for example, the heat-resistant layer **27** is provided on both surfaces of the separator **23**. One reason for this is that, as described later, if the heat-resistant layer **27** is provided on both surfaces of the separator **23**, handling thereof is easier and manufacturing steps of the secondary battery becomes easier compared to a case in which the heat-resistant layer **27** is provided on the cathode **21** or the anode **22**. Thereby, the heat-resistant layer **27** is located between the cathode **21** and the separator **23** and between the anode **22** and the separator **23**. The "both surfaces of the separator **23**" refer to the surface of the separator **23** on the side opposed to the cathode **21** and the surface of the separator **23** on the side opposed to the anode **22**.

The heat-resistant layer **27** prevents occurrence of unintentional conduction (short circuit) between the cathode **21** and the anode **22**, and contains a material (hereinafter referred to as "heat-resistant material") having a higher melting point or higher decomposition temperature than the melting point or the decomposition temperature of the separator **23**. One reason for this is that, in this case, even if the separator **23** is melted or fused under high temperature conditions resulting from heat generation of the secondary battery, the cathode **21** and the anode **22** are prevented from being physically contacted with each other.

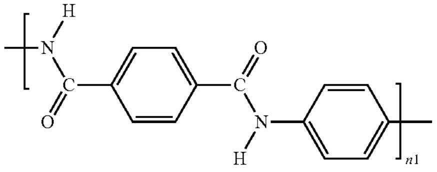
Type of the heat-resistant material is not particularly limited as long as a material having a higher melting point or higher decomposition temperature than the melting point or the decomposition temperature of the separator **23** is used. In particular, the melting point or the decomposition temperature of the heat-resistant material is preferably equal to or more than about 200 deg C., and is more preferably from about 210 deg C. to about 2100 deg C. both inclusive. One reason for this is as follows. As a material for forming the separator **23**, a polymer compound is generally used. Therefore, in the case where the melting point or the decomposition temperature of the heat-resistant layer **27** is within the foregoing range, the condition "having a higher melting point or higher decomposition temperature than the melting point or the decomposition temperature of the separator **23**" is easily satisfied. Another reason for this is that in a lithium ion secondary battery, in general, thermal runaway easily occurs at temperature equal to or more than about 200 deg C. In some cases, temperature at which thermal runaway occurs in a lithium ion secondary battery varies according to combination of a cathode active material and an anode active material. Specifically, for example, in the case where the cathode active material is a lithium-containing compound having a bedded salt-type crystal structure or the like and an anode active material is a material capable of inserting and extracting lithium ions or the like, thermal runaway easily occurs. Examples of the lithium-containing compound having a bedded salt-type crystal structure include the foregoing lithium-transition-metal composite oxide such as $LiCo_2$. Examples of the material capable of inserting and extracting lithium ions include the foregoing carbon material and the foregoing metal-based material. Therefore, the state that the melting point or the decomposition temperature of the heat-resistant material is equal to or more than about 200 deg C. is effective in the lithium ion secondary battery in which thermal runaway easily occurs.

Specific examples of the heat-resistant material include a polymer compound, since superior heat stability is thereby obtained, and the heat-resistant layer **27** is easily formed thereby.

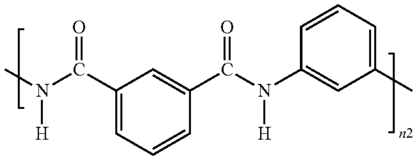
Examples of the polymer compound include one or more of polymer materials such as polyamide, polystyrene, polymethyl methacrylate, polycarbonate, polyethylene terephthalate, polybutylene terephthalate, polyphenylene sulfide, polysulfone, polyethersulfone, polyether ether ketone, polytetrafluoroethylene, polyimide, polyether imide, melamine, benzoguanamine, and polytetrafluoroethylene, since such polymer materials have superior heat stability. Polyamide may be aliphatic or aromatic.

In particular, a polymer material having an amide bond (—C(═O)—NH—) is preferable, since the polymer material having an amide bond generally has a melting point or decomposition temperature more than 200 deg C. Type (chemical formula) of the polymer material having an amide bond is not particularly limited. However, for example, the type of the polymer material having an amide bond may be one or more of an aliphatic polyamide and an aromatic polyamide, and the aromatic polyamide is more preferable, since more superior heat stability is thereby obtained. More specific examples of the aromatic polyamide include a para-type (p-) aromatic polyamide represented by the following Formula (30-1) and a meta-type (m-) aromatic polyamide represented by the following Formula (30-2). As melting points or decomposition temperature of the representative polymer materials, the melting point or the decomposition temperature of the para-type aromatic polyamide is about 600 deg C., and the melting point or the decomposition temperature of the meta-type aromatic polyamide is more than 600 deg C. (unmeasurable).

(30-1)



(30-2)



In Formulas (30-1) and (30-2), n1 and n2 are each one of integer numbers from 100 to 10000 both inclusive.

In the case where the heat-resistant material is a polymer compound, the heat-resistant layer **27** containing such a heat-resistant material is formed by, for example, a coating method. In this case, for example, after the polymer compound is dissolved in an organic solvent or the like, the separator **23** is coated with the solution, the resultant is dried, and a polymer compound film is thereby formed.

Alternatively, for example, the heat-resistant material is an oxide, since superior heat stability is thereby obtained, and the heat-resistant layer **27** is easily formed thereby.

Examples of the oxide include one or more of oxides of Group 4 elements, Group 13 elements, and Group 14 elements in the long-period-type periodic table, since melting points of the oxides of these elements are generally more than 200 deg C. more specifically, examples of the oxide include one or more of metal-based oxides (or inorganic oxides) such as aluminum oxide, titanium oxide, silicon oxide, and zirconium oxide. In particular, aluminum oxide, titanium oxide, and silicon oxide are preferable, and aluminum oxide is more preferable, since superior heat stability is thereby obtained. As melting points or decomposition temperature of the representative oxides, the melting point or the decomposition temperature of aluminum oxide is about 2054 deg C., the melting point or the decomposition temperature of titanium oxide is about 1870 deg C., and the melting point or the decomposition temperature of silicon oxide is about 1650 deg C.

The average particle diameter (median diameter) of the oxide is not particularly limited. However, in particular, the average particle diameter thereof is preferably from 0.001 μm to 10 μm both inclusive, and is more preferably from 0.01 μm to 1 μm both inclusive, since in this case, the heat-resistant layer **27** is thereby thinned while permeability of the electrolytic solution is secured.

In the case where the heat-resistant material is an oxide, the heat-resistant layer **27** preferably contains the oxide and a polymer compound (retaining polymer compound) for retaining the oxide, since in this case, the heat-resistant layer **27** is allowed to keep dispersion state of a plurality of oxide particles.

Type of the retaining polymer compound is not particularly limited as long as a compound capable of retaining an oxide is used. Examples of the retaining polymer compound include one or more of polymer materials such as polyamide, polystyrene, polymethyl methacrylate, polycarbonate, polyethylene terephthalate, polybutylene terephthalate, polyphenylene sulfide, polysulfone, polyethersulfone, polyether ether ketone, polytetrafluoroethylene, polyimide, polyether imide, melamine, benzoguanamine, polytetrafluoroethylene, and polyvinylidene fluoride.

In this case, since a function (heat resistance) of the heat-resistant layer **27** is exercised by the oxide as a heat-resistant material, the retaining polymer compound does not necessarily have heat resistance. That is, in the case where the heat-resistant layer **27** contains the oxide as a heat-resistant material, the melting point or the decomposition temperature of the retaining polymer compound is not particularly limited. Therefore, the melting point or the decomposition temperature of the retaining polymer compound may be lower than the melting point or the decomposition temperature of the separator **23**. However, in order to further prevent occurrence of short circuit, the melting point or the decomposition temperature of the retaining polymer compound is preferably higher than the melting point or the decomposition temperature of the separator **23** as well.

In the case where the heat-resistant material is an oxide, the heat-resistant layer **27** containing such a heat-resistant material is formed by, for example, a coating method. In this case, for example, the retaining polymer compound is dissolved in an organic solvent or the like, and as necessary, other materials are dispersed in a solution thereof together with particles of the oxide. Subsequently, the separator **23** is coated with the solution, and the resultant is dried. Thereby, a polymer compound film containing the particles of the oxide is formed. The content of the oxide in the solution is not particularly limited. However, defects such as repelling at the time of coating are allowed to be resolved by adjusting the content (so-called concentration) of the oxide.

Examples of the foregoing other materials include a surface-active agent. The content of the surface-active agent in the solution is not particularly limited. However, the content thereof is preferably from 0.01 wt % to 3 wt % both inclusive, and is more preferably from 0.05 wt % to 1 wt % both inclusive, since in this case, dispersibility, coating characteristics (wetting characteristics) and/or the like are improved thereby.

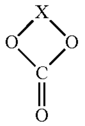
When the heat-resistant layer **27** containing the retaining polymer compound together with the oxide is formed, for example, the polymer compound is concentrated in the vicinity of a contact interface between oxide particles or in the vicinity of a contact interface between an oxide particle and a particle of the anode active material layer. Thereby, the polymer compound exists sparsely in portions other than the foregoing portion in the vicinity of the contact interface, and as a result, spaces (fine pores) are formed in such portions. Therefore, the heat-resistant layer **27** may have a porous structure (porous interconnection structure). Accordingly, even if the heat-resistant layer **27** is provided on the separator **23**, the separator **23** is easily impregnated with an electrolytic solution.

The thickness of the heat-resistant layer **27** is not particularly limited. However, in particular, the thickness is preferably from 0.1 μm to 10 μm both inclusive, and is more preferably from 0.5 μm to 5 μm both inclusive, since in this case, superior heat resistivity is thereby obtained while increase of electric resistance is suppressed. Further, though the density of the heat-resistant layer **27** is not particularly limited, in particular, the density thereof is preferably from 0.01 mg/cm^2 to 10 mg/cm^2 both inclusive for a reason similar to that of the foregoing thickness.

As described above, it is enough that the heat-resistant layer **27** is provided at least in the opposed region R. Therefore, the formation range of the heat-resistant layer **27** may be only the opposed region R, or may be expanded to a region around the opposed region R in addition to the opposed region R. FIG. **3** illustrates a case that the heat-resistant layer **27** is provided in a region around the opposed region R in addition to the opposed region R, and in particular, a case that the formation range of the heat-resistant layer **27** is extended toward the inner side and the outer side of the spirally wound body, the formation range of the heat-resistant layer **27** being beyond the formation range of the anode active material layer **22**B.

[Electrolytic Solution]

The separator **23** is impregnated with an electrolytic solution as a liquid electrolyte. The electrolytic solution contains one or more of unsaturated cyclic ester carbonates represented by the following Formula (1) (hereinafter, simply referred to as "unsaturated cyclic ester carbonate"). However, the electrolytic solution may contain other material such as a solvent and an electrolyte salt.



(1)

In Formula (1), X is a divalent group in which m-number of >C═CR1R2 and n-number of >CR3R4 are bonded in any order. Each of R1 to R4 is one of a hydrogen group, a halogen group, a monovalent hydrocarbon group, a monovalent halogenated hydrocarbon group, a monovalent oxygen-containing hydrocarbon group, and a monovalent halogenated oxygen-containing hydrocarbon group. Any two or more of R1 to R4 may be bonded to each other. m and n satisfy m≥1 and n≥0.

The unsaturated cyclic ester carbonate refers to a cyclic ester carbonate having one or more unsaturated bonds (>C═C< as carbon-carbon double bonds). One reason why the electrolytic solution contains the unsaturated cyclic ester carbonate is that, in the case where the heat-resistant layer **27** having a higher melting point than that of the separator **23** is provided on the anode **22**, and the electrolytic solution contains the unsaturated cyclic ester carbonate, occurrence of short circuit is suppressed and the chemical stability of the electrolytic solution is improved.

More specifically, in the case where the melting point or the decomposition temperature of the heat-resistant layer **27** is equal to or less than the melting point or the decomposition temperature of the separator **23**, even if the electrolytic solution contains the unsaturated cyclic ester carbonate, the chemical stability of the electrolytic solution is not substantially improved. One reason for this may be that, if the separator **23** is, for example, melted at the time of charge and discharge, short circuit occurs, and therefore, a function of suppressing decomposition of the electrolytic solution by the unsaturated cyclic ester carbonate is not sufficiently exercised.

On the other hand, in the case where the melting point or the decomposition temperature of the heat-resistant layer **27** is more than the melting point or the decomposition temperature of the separator **23**, if the electrolytic solution contains the unsaturated cyclic ester carbonate, the chemical stability of the electrolytic solution is improved. One reason for this may be that, even if the separator **23** is, for example, melted at the time of charge and discharge, occurrence of short circuit is suppressed by the heat-resistant layer **27**, and a function of suppressing decomposition of the electrolytic solution by the unsaturated cyclic ester carbonate is sufficiently exercised. Such a tendency that the chemical stability of the electrolytic solution is improved is significant under strict conditions such as a high-temperature environment.

X in Formula (1) is a group obtained by bonding m-number of >C═CR1R2 to n-number of >CR3R4 so that the valency becomes divalent as a whole (one bonding hand exists on each of both ends). Adjacent groups (groups bonded to each other) may be the same type of group such as >C═CR1R2 and >C═CR1R2, or may be different from each other such as >C═CR1-R2 and >CR3R4. That is, the number (m) of >C═CR1R2 used for forming the divalent group and the number (n) of >CR3R4 used for forming the divalent group may be any number, and the bonding order thereof may also be any order.

While >C═CR1R2 is a divalent unsaturated group having the foregoing carbon-carbon double bond, >CR3R4 is a divalent saturated group not having a carbon-carbon double bond. Since n satisfies n≥0, >CR3R4 as a saturated group may be included in X, and is not necessarily included in X. On the other hand, since m satisfies m≥1, it may be necessary to include one or more >C═CR1R2 as an unsaturated group in X typically. Therefore, X may be configured of only >C═CR1R2, or may be configured of both >C═CR1R2 and >CR3R4. One reason for this is that it may be necessary to include one or more unsaturated groups in a chemical structure of the unsaturated cyclic ester carbonate.

Values of m and n are not particularly limited as long as the conditions of m≥1 and n≥0 are satisfied. In particular, in the case where >C═CR1R2 is >C═CH_2 and >CR3R4 is >CH_2, (m+n)≤5 is preferably satisfied. One reason for this is that, in this case, the carbon number of X is not excessively large, and therefore, the solubility and the compatibility of the unsaturated cyclic ester carbonate are secured.

It is to be noted that any two or more of R1 to R4 in >C═CR1R2 and >CR3R4 may be bonded to one another, and the bonded groups may form a ring. As an example, R1 may be bonded to R2, R3 may be bonded to R4, and R2 may be bonded to R3 or R4.

Details of R1 to R4 are described below. R1 to R4 may be the same type of group, or may be groups different from one another. Any two or three of R1 to R4 may be the same type of group.

Each type of R1 to R4 is not particularly limited as long as each of R1 to R4 is one of a hydrogen group, a halogen group, a monovalent hydrocarbon group, a monovalent halogenated hydrocarbon group, a monovalent oxygen-containing hydrocarbon group, and a monovalent halogenated oxygen-containing hydrocarbon group. One reason for this is that, since, in this case, X has one or more carbon-carbon double bonds (>C═CR1R2), the foregoing advantage is obtainable without depending on the types of R1 to R4.

The halogen group is, for example, one or more of a fluorine group (—F), a chlorine group (—Cl), a bromine group (—Br), an iodine group (—I), and the like. In particular, the fluorine group is preferable, since a higher effect is thereby obtainable.

"Monovalent hydrocarbon group" is a generic term used to refer to monovalent groups configured of C and H, and may have a straight-chain structure or a branched structure having one or more side chains. Examples of the monovalent hydrocarbon group include an alkyl group with carbon number from 1 to 12 both inclusive, an alkenyl group with carbon number from 2 to 12 both inclusive, an alkynyl group with carbon number from 2 to 12 both inclusive, an aryl group with carbon number from 6 to 18 both inclusive, and a cycloalkyl group with carbon number from 3 to 18 both inclusive. One reason for this is that the foregoing advantage is thereby obtained while the solubility, the compatibility, and the like of the unsaturated cyclic ester carbonate are secured.

More specific examples of the alkyl group include a methyl group (—CH_3), an ethyl group (—C_2H_5), and a propyl group (—C_3H_7). Examples of the alkenyl group include a vinyl group (—CH═CH_2) and an allyl group (—CH_2—CH═CH_2). Examples of the alkynyl group include an ethynyl group (—C≡CH). Examples of the aryl group include a phenyl group and a naphtyl group. Examples of the cycloalkyl group include a cyclopropyl group, a cyclobutyl group, a cyclopentyl group, a cyclohexyl group, a cycloheptyl group, and a cyclooctyl group.

"Monovalent oxygen-containing hydrocarbon group" is a generic term used to refer to monovalent groups configured of 0 together with C and H. Examples of the monovalent oxygen-containing hydrocarbon group include an alkoxy group with carbon number from 1 to 12 both inclusive. One reason for this is that the foregoing advantage is thereby obtained while the solubility, the compatibility, and the like of the unsaturated cyclic ester carbonate are secured. More specific examples of the alkoxy group include a methoxy group (—OCH_3) and an ethoxy group (—OC_2H_5).

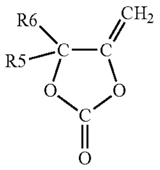
A group obtained by bonding two or more of the foregoing alkyl group and the like so that the whole valency becomes monovalent may be used. Examples thereof include a group obtained by bonding an alkyl group to an aryl group and a group obtained by bonding an alkyl group to a cycloalkyl group. More specific examples of the group obtained by bonding an alkyl group to an aryl group include a benzil group.

"Monovalent halogenated hydrocarbon group" is obtained by substituting (halogenating) each of part or all of hydrogen groups (—H) out of the foregoing monovalent hydrocarbon group by a halogen group. Similarly, "monovalent halogenated oxygen-containing hydrocarbon group" is obtained by substituting each of part or all of hydrogen groups out of the foregoing monovalent oxygen-containing hydrocarbon group by a halogen group. In either case, types of the halogen group substituting for a hydrogen group are similar to the types of the halogen group described above.

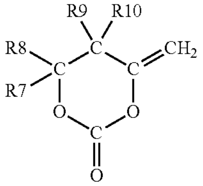
Examples of the monovalent halogenated hydrocarbon group include a group obtained by halogenating the foregoing alkyl group or the like. That is, the monovalent halogenated hydrocarbon group is a group obtained by substituting each of part or all of hydrogen groups of the foregoing alkyl group or the like by a halogen group. More specific examples of the group obtained by halogenating an alkyl group or the like include a trifluoromethyl group (—CF_3) and a pentafluoroethyl group (—C_2F_5). Further, examples of the monovalent halogenated oxygen-containing hydrocarbon group include a group obtained by substituting each of part or all of hydrogen groups of the foregoing alkoxy group or the like by a halogen group. More specific examples of the group obtained by halogenating an alkoxy group or the like include a trifluoromethoxy group (—OCF_3) and a pentafluoroethoxy group (—OC_2F_5).

It is to be noted that each of R1 to R4 may be a group other than the foregoing groups. Specifically, each of R1 to R4 may be, for example, a derivative of each of the foregoing groups. The derivative is obtained by introducing one or more substituent groups to each of the foregoing groups. Substituent group types may be any type.

In particular, the unsaturated cyclic ester carbonate is preferably represented by the following Formula (2) or the following Formula (3). One reason for this is that, in this case, the foregoing advantage is obtained, and such compounds are easily synthesized.



(2)



(3)

In Formulas (2) and (3), each of R5 to R10 is one of a hydrogen group, a halogen group, a monovalent hydrocarbon group, a monovalent halogenated hydrocarbon group, a monovalent oxygen-containing hydrocarbon group, and a monovalent halogenated oxygen-containing hydrocarbon group. R5 and R6 may be bonded to each other; and any two or more of R7 to R10 may be bonded to one another.

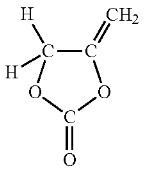
Focusing attention on a relation between Formula (1) and Formula (2), the unsaturated cyclic ester carbonate represented by Formula (2) has, as X in Formula (1), one unsaturated group (>C═CH_2) corresponding to

>C═CR1R2 and one saturated group (>CR5R6) corresponding to >CR3R4. On the other hand, focusing attention on a relation between Formula (1) and Formula (3), the unsaturated cyclic ester carbonate represented by Formula (3) has, as X, one unsaturated group (>C═CH_2) corresponding to >C═CR1R2 and two saturated groups (>CR7R8 and >CR9R10) corresponding to >CR3R4. However, the foregoing one unsaturated group and the foregoing two saturated groups are bonded in order of >CR7R8, >CR9R10, and C═CH_2.

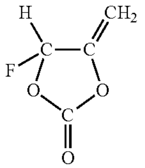
Details of R5 and R6 in Formula (2) and R7 to R10 in Formula (3) are similar to those of R1 to R4 in Formula (1), and therefore, descriptions thereof will be omitted.

Specific examples of the unsaturated cyclic ester carbonate include compounds represented by the following Formula (1-1) to the following Formula (1-56). Such unsaturated cyclic ester carbonates include a geometric isomer. However, specific examples of the unsaturated cyclic ester carbonate are not limited to the compounds listed in Formula (1-1) to Formula (1-56).

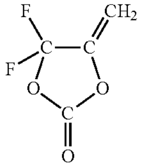
(1-1)



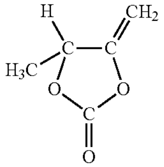
(1-2)



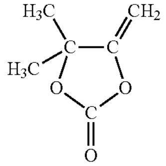
(1-3)



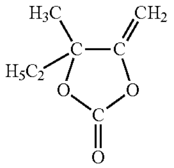
(1-4)



(1-5)

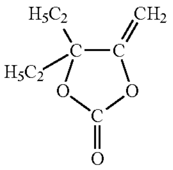


(1-6)

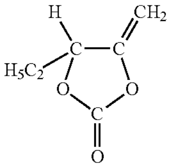


-continued

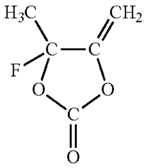
(1-7)



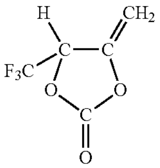
(1-8)



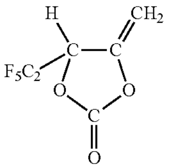
(1-9)



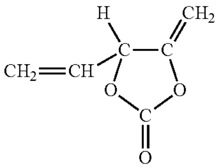
(1-10)



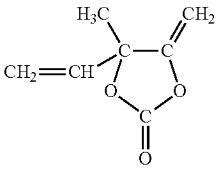
(1-11)



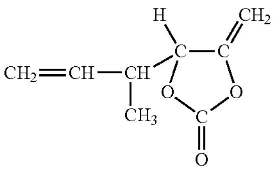
(1-12)



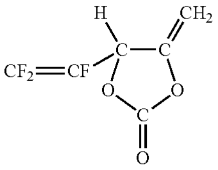
(1-13)



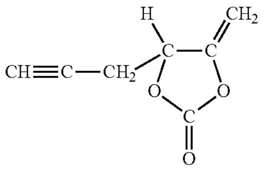
(1-14)



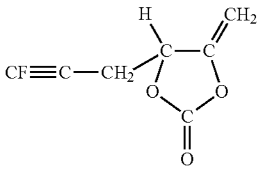
(1-15)



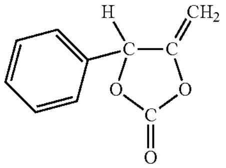
-continued



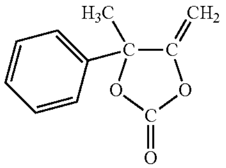
(1-16)



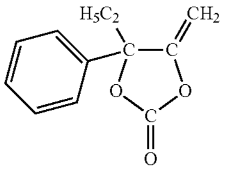
(1-17)



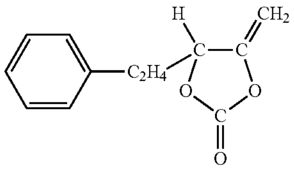
(1-18)



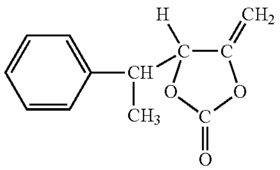
(1-19)



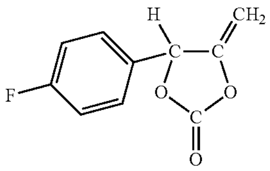
(1-20)



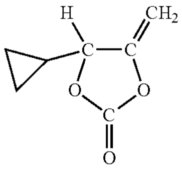
(1-21)



(1-22)

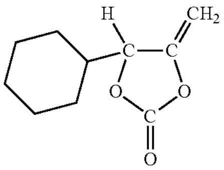


(1-23)

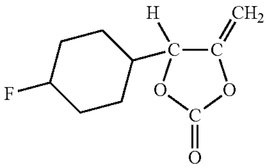


(1-24)

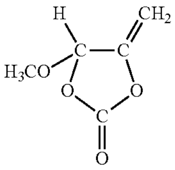
-continued



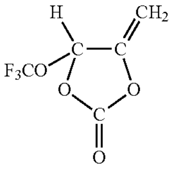
(1-25)



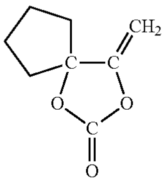
(1-26)



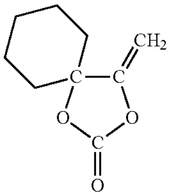
(1-27)



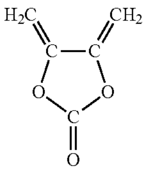
(1-28)



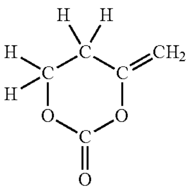
(1-29)



(1-30)



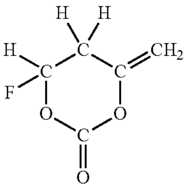
(1-31)



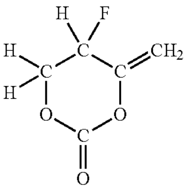
(1-32)

-continued

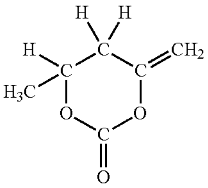
(1-33)



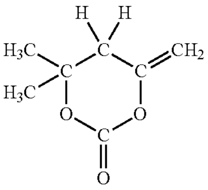
(1-34)



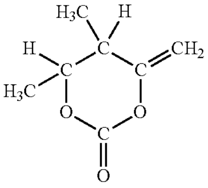
(1-35)



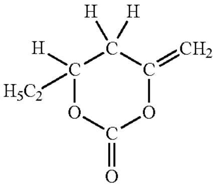
(1-36)



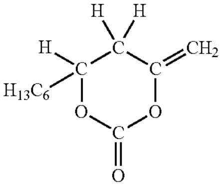
(1-37)



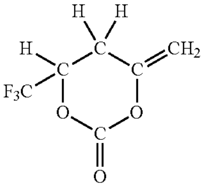
(1-38)



(1-39)

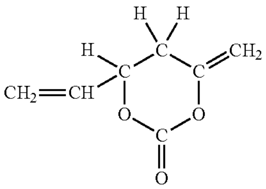


(1-40)

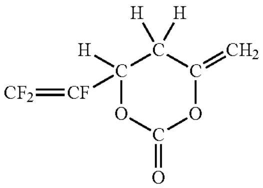


-continued

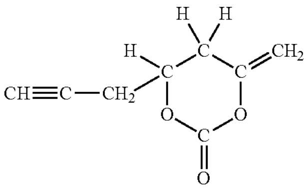
(1-41)



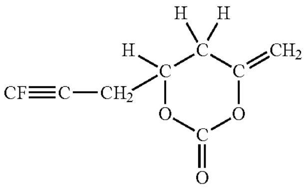
(1-42)



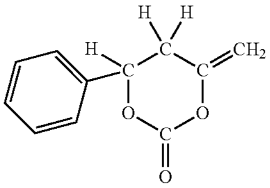
(1-43)



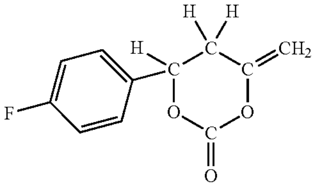
(1-44)



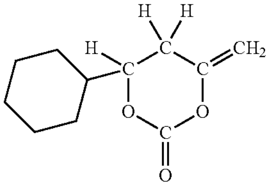
(1-45)



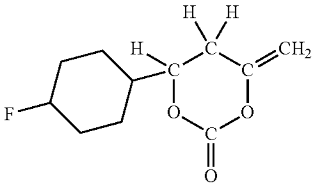
(1-46)



(1-47)

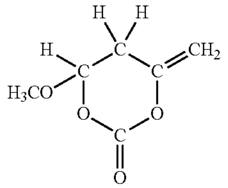


(1-48)

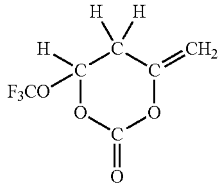


-continued

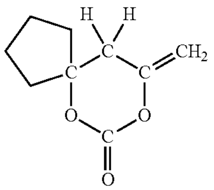
(1-49)



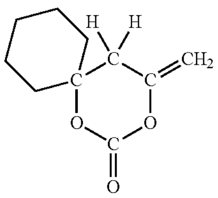
(1-50)



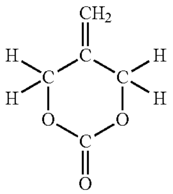
(1-51)



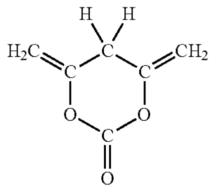
(1-52)



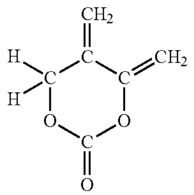
(1-53)



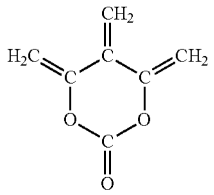
(1-54)



(1-55)



(1-56)



In particular, Formula (1-1) and the like corresponding to Formula (2) or Formula (1-32) and the like corresponding to Formula (3) are preferable, since a higher effect is thereby obtainable.

Although the content of the unsaturated cyclic ester carbonate in the electrolytic solution is not particularly limited, in particular, the content thereof is preferably from 0.01 wt % to 10 wt % both inclusive, more preferably from 1 wt % to 10 wt % both inclusive, and further more preferably from 2 wt % to 5 wt % both inclusive, since a higher effect is thereby obtainable.

The solvent used for the electrolytic solution contains one or more of nonaqueous solvents such as an organic solvent (excluding the foregoing unsaturated cyclic ester carbonate).

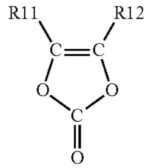
Examples of the nonaqueous solvents include a cyclic ester carbonate, a chain ester carbonate, lactone, a chain carboxylic ester, and nitrile, since thereby, a superior battery capacity, superior cycle characteristics, superior conservation characteristics, and the like are obtained. Examples of the cyclic ester carbonate include ethylene carbonate, propylene carbonate, and butylene carbonate. Examples of the chain ester carbonate include dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, and methylpropyl carbonate. Examples of the lactone include γ-butyrolactone and γ-valerolactone. Examples of the carboxylic ester include methyl acetate, ethyl acetate, methyl propionate, ethyl propionate, methyl butyrate, methyl isobutyrate, methyl trimethylacetate, and ethyl trimethylacetate. Examples of the nitrile include acetonitrile, glutaronitrile, adiponitrile, methoxyacetonitrile, and 3-methoxypropionitrile.

In addition thereto, the nonaqueous solvent may be, for example, 1,2-dimethoxyethane, tetrahydrofuran, 2-methyltetrahydrofuran, tetrahydropyran, 1,3-dioxolane, 4-methyl-1,3-dioxolane, 1,3-dioxane, 1,4-dioxane, N,N-dimethylformamide, N-methylpyrrolidinone, N-methyloxazolidinone, N,N'-dimethylimidazolidinone, nitromethane, nitroethane, sulfolane, trimethyl phosphate, and dimethyl sulfoxide. Thereby, a similar advantage is obtained.

In particular, one or more of ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, and ethyl methyl carbonate are preferable, since thereby, a superior battery capacity, superior cycle characteristics, superior conservation characteristics, and the like are obtained. In this case, a combination of a high viscosity (high dielectric constant) solvent (for example, specific dielectric constant $\varepsilon \geqq 30$) such as ethylene carbonate and propylene carbonate and a low viscosity solvent (for example, viscosity$\leqq$1 mPa·s) such as dimethyl carbonate, ethylmethyl carbonate, and diethyl carbonate is more preferable. One reason for this is that the dissociation property of the electrolyte salt and ion mobility are improved.

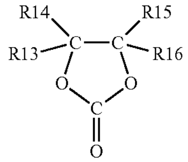
In particular, the solvent preferably contains one or more of other unsaturated cyclic ester carbonates represented by the following Formula (4) and the following Formula (5). One reason for this is that a stable protective film is formed mainly on the surface of the anode **22** at the time of charge and discharge, and therefore, a decomposition reaction of the electrolytic solution is suppressed. R11 and R12 may be the same type of group, or may be groups different from each other. Further, R13 to R16 may be the same type of group, or may be groups different from one another. Alternatively, part of R13 to R16 may be the same type of group. The content of other unsaturated cyclic ester carbonate in the solvent is not particularly limited, and is, for example, from 0.01 wt % to 10 wt % both inclusive. However, specific examples of other unsaturated cyclic ester carbonate are not limited to the after-mentioned compounds.

(4)



In Formula (4), each of R11 and R12 is one of a hydrogen group and an alkyl group.

(5)



In Formula (5), each of R13 to R16 is one of a hydrogen group, an alkyl group, a vinyl group, and an allyl group. One or more of R13 to R16 each are a vinyl group or an allyl group.

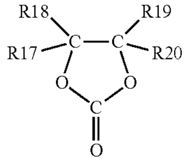
Other unsaturated cyclic ester carbonate represented by Formula (4) is a vinylene-carbonate-based compound. Each type of R11 and R12 is not particularly limited as long as each of R11 and R12 is one of a hydrogen group and an alkyl group. Examples of the alkyl group include a methyl group and an ethyl group, and the carbon number of the alkyl group is preferably from 1 to 12 both inclusive, since superior solubility and superior compatibility are thereby obtained. Specific examples of the vinylene-carbonate-based compounds include vinylene carbonate (1,3-dioxole-2-one), methylvinylene carbonate (4-methyl-1,3-dioxole-2-one), ethylvinylene carbonate (4-ethyl-1,3-dioxole-2-one), 4,5-dimethyl-1,3-dioxole-2-one, and 4,5-diethyl-1,3-dioxole-2-one. It is to be noted that each of R11 and R12 may be a group obtained by substituting each of part or all of hydrogen groups of the alkyl group by a halogen group. In this case, specific examples of the vinylene carbonate-based compounds include 4-fluoro-1,3-dioxole-2-one and 4-trifluoromethyl-1,3-dioxole-2-one. In particular, vinylene carbonate is preferable, since vinylene carbonate is easily available and provides a high effect.

Other unsaturated cyclic ester carbonate represented by Formula (5) is a vinylethylene-carbonate-based compound. Each type of R13 to R16 is not particularly limited as long as each of R13 to R16 is one of a hydrogen group, an alkyl group, a vinyl group, and an allyl group, where one or more of R13 to R16 are each one of a vinyl group and an allyl group. The type and the carbon number of the alkyl group are similar to those of R11 and R12. Specific examples of the vinylethylene-carbonate-based compounds include vinylethylene carbonate (4-vinyl-1,3-dioxolane-2-one), 4-methyl-4-vinyl-1,3-dioxolane-2-one, 4-ethyl-4-vinyl-1,3-dioxolane-2-one, 4-n-propyl-4-vinyl-1,3-dioxolane-2-one, 5-methyl-4-vinyl-1,3-dioxolane-2-one, 4,4-divinyl-1,3-dioxolane-2-one, and 4,5-divinyl-1,3-dioxolane-2-one. In particular, vinylethylene carbonate is preferable, since vinylethylene carbonate is easily available, and provides a high effect. It goes without saying that all of R13 to R16 may be vinyl groups or allyl groups. Alternatively, some of R13 to R16 may be vinyl groups, and the others thereof may be allyl groups.

It is to be noted that other unsaturated cyclic ester carbonate may be the compounds represented by Formula (4) and Formula (5), or may be catechol carbonate having a benzene ring.

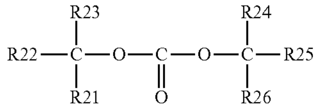
Further, the solvent preferably contains one or more of halogenated ester carbonates represented by the following Formula (6) and the following Formula (7). One reason for this is that a stable protective film is formed mainly on the surface of the anode **22** at the time of charge and discharge, and therefore, a decomposition reaction of the electrolytic solution is suppressed. The halogenated ester carbonate represented by Formula (6) is a cyclic ester carbonate having one or more halogens as constituent elements (halogenated cyclic ester carbonate). The halogenated ester carbonate represented by Formula (7) is a chain ester carbonate having one or more halogens as constituent elements (halogenated chain ester carbonate). R17 to R20 may be the same type of group, or may be groups different from one another. Alternatively, part of R17 to R20 may be the same type of group. The same is applied to R21 to R26. Although the content of the halogenated ester carbonate in the solvent is not particularly limited, the content thereof is, for example, from 0.01 wt % to 50 wt % both inclusive. However, specific examples of the halogenated ester carbonate are not limited to the compounds described below.

(6)



In Formula (6), each of R17 to R20 is one of a hydrogen group, a halogen group, an alkyl group, and a halogenated alkyl group. One or more of R17 to R20 are each one of a halogen group and a halogenated alkyl group.

(7)



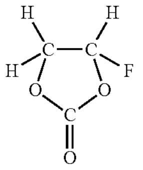
$$R22-\underset{R21}{\overset{R23}{C}}-O-\underset{O}{\overset{}{\underset{\|}{C}}}-O-\underset{R26}{\overset{R24}{C}}-R25$$

In Formula (7), each of R21 to R26 is one of a hydrogen group, a halogen group, an alkyl group, and a halogenated alkyl group. One or more of R21 to R26 are each a halogen group or a halogenated alkyl group.

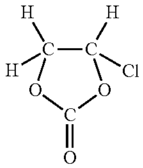
Although halogen type is not particularly limited, in particular, fluorine (F), chlorine (Cl), or bromine (Br) is preferable, and fluorine is more preferable since thereby, a higher effect is obtained compared to other halogens. However, the number of halogens is more preferably two than one, and further may be three or more. One reason for this is that, since thereby, an ability of forming a protective film is improved, a more rigid and stable protective film is formed.

Examples of the halogenated cyclic ester carbonate include compounds represented by the following Formula (6-1) to the following Formula (6-21). Such compounds include a geometric isomer. In particular, 4-fluoro-1,3-dioxolane-2-one represented by Formula (6-1) or 4,5-difluoro-1,3-dioxolane-2-one represented by Formula (6-3) is preferable, and the latter is more preferable. Further, as 4,5-difluoro-1,3-dioxolane-2-one, a trans isomer is more preferable than a cis isomer, since the trans isomer is easily available and provides a high effect. Examples of the halogenated chain ester carbonate include fluoromethyl methyl carbonate, bis(fluoromethyl) carbonate, and difluoromethyl methyl carbonate.

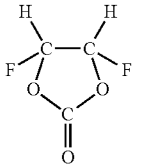
(6-1)



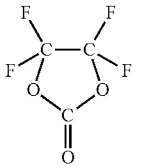
(6-2)



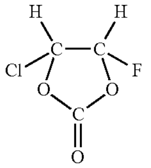
(6-3)



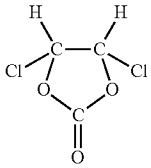
(6-4)



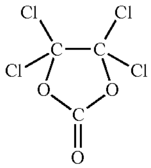
(6-5)



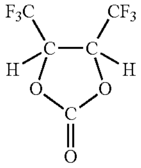
(6-6)



(6-7)

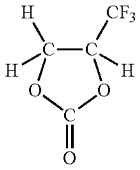


(6-8)

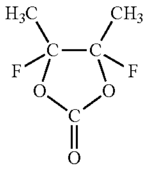


-continued

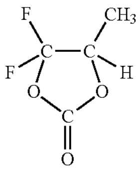
(6-9)



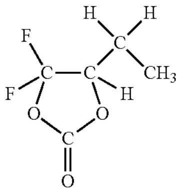
(6-10)



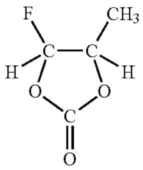
(6-11)



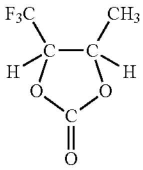
(6-12)



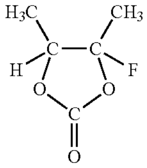
(6-13)



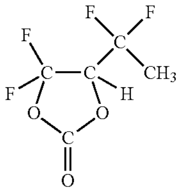
(6-14)



(6-15)

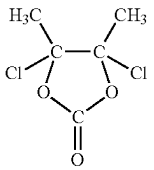


(6-16)

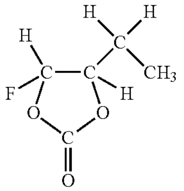


-continued

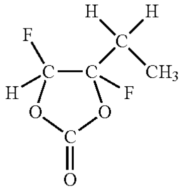
(6-17)



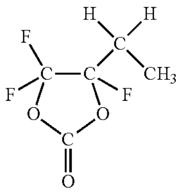
(6-18)



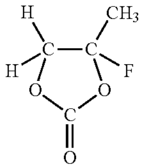
(6-19)



(6-20)



(6-21)



Further, the solvent preferably contains sultone (cyclic sulfonic ester), since the chemical stability of the electrolytic solution is more improved thereby. Examples of sultone include propane sultone and propene sultone. Although the sultone content in the solvent is not particularly limited, for example, the sultone content is from 0.5 wt % to 5 wt % both inclusive. Specific examples of sultone are not limited to the foregoing compounds, and other compound may be used.

Further, the solvent preferably contains an acid anhydride since the chemical stability of the electrolytic solution is thereby further improved. Examples of the acid anhydrides include a carboxylic anhydride, a disulfonic anhydride, and a carboxylic acid sulfonic acid anhydride. Examples of the carboxylic anhydride include a succinic anhydride, a glutaric anhydride, and a maleic anhydride. Examples of the disulfonic anhydride include an ethane disulfonic anhydride and a propane disulfonic anhydride. Examples of the carboxylic acid sulfonic acid anhydride include a sulfobenzoic anhydride, a sulfopropionic anhydride, and a sulfobutyric anhydride. Although the content of the acid anhydride in the solvent is not particularly limited, for example, the content thereof is from 0.5 wt % to 5 wt % both inclusive. However, specific examples of the acid anhydrides are not limited to the foregoing compounds, and other compound may be used.

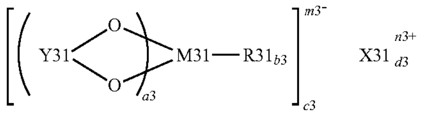
The electrolyte salt used for the electrolytic solution may contain, for example, one or more of salts such as a lithium salt. However, the electrolyte salt may contain, for example, a salt other than the lithium salt (for example, a light metal salt other than the lithium salt).

Examples of the lithium salts include lithium hexafluorophosphate ($LiPF_6$), lithium tetrafluoroborate ($LiBF_4$), lithium perchlorate ($LiClO_4$), lithium hexafluoroarsenate ($LiAsF_6$), lithium tetraphenylborate ($LiB(C_6H_5)_4$), lithium methanesulfonate ($LiCH_3SO_3$), lithium trifluoromethane sulfonate ($LiCF_3SO_3$), lithium tetrachloroaluminate ($LiAlCl_4$), dilithium hexafluorosilicate (Li_2SiF_6), lithium chloride (LiCl), and lithium bromide (LiBr). Thereby, a superior battery capacity, superior cycle characteristics, superior conservation characteristics, and the like are obtained. However, specific examples of the lithium salt are not limited to the foregoing compounds, and may be other compounds.

In particular, one or more of $LiPF_6$, $LiBF_4$, $LiClO_4$, and $LiAsF_6$ are preferable, and $LiPF_6$ is more preferable, since the internal resistance is thereby lowered, and therefore, a higher effect is obtained.

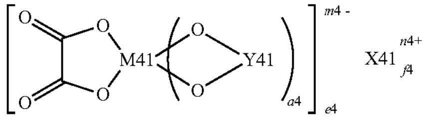
In particular, the electrolyte salt preferably contains one or more of compounds represented by the following Formula (8) to the following Formula (10), since a higher effect is obtained thereby. It is to be noted that R31 and R33 may be the same type of group, or may be groups different from each other. The same is applied to R41 to R43 and to R51 and R52. However, specific examples of the compounds represented by Formula (8) to Formula (10) are not limited to the after-mentioned compounds.

(8)



In Formula (8), X31 is one of Group 1 elements, Group 2 elements in the long-period periodic table, and Al. M31 is one of transition metals, Group 13 elements, Group 14 elements, and Group 15 elements in the long-period periodic table. R31 is a halogen group. Y31 is one of —C(=O)—R32-C(=O)—, —C(=O)—CR33$_2$, and —C(=O)—C(=O)—. R32 is one of an alkylene group, a halogenated alkylene group, an arylene group, and a halogenated arylene group. R33 is one of an alkyl group, a halogenated alkyl group, an aryl group, and a halogenated aryl group. a3 is one of integer numbers 1 to 4 both inclusive. b3 is one of integer numbers 0, 2, and 4. Each of c3, d3, m3, and n3 is one of integer numbers 1 to 3 both inclusive.

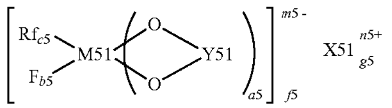
(9)



In Formula (9), X41 is one of Group 1 elements and Group 2 elements in the long-period periodic table. M41 is one of transition metals, Group 13 elements, Group 14 elements, and Group 15 elements in the long-period periodic table. Y41 is one of —C(=O)—(CR41$_2$)$_{b4}$—C(=O)—, —R43$_2$C—(CR42$_2$)$_{c4}$—C(=O)—, —R43$_2$C—(CR42$_2$)$_{c4}$—CR43$_2$—, —R43$_2$C—(CR42$_2$)$_{c4}$—S(=O)$_2$—, —S(=O)$_2$—(CR42$_2$)$_{d4}$—S(=O)$_2$—, and —C(=O)—

$(CR42_2)_{d4}$—S(=O)$_2$—. Each of R41 and R43 is one of a hydrogen group, an alkyl group, a halogen group, and a halogenated alkyl group. One or more of R41 and R43 are each the halogen group or the halogenated alkyl group. R42 is one of a hydrogen group, an alkyl group, a halogen group, and a halogenated alkyl group. Each of a4, e4, and n4 is one of integer numbers 1 and 2. Each of b4 and d4 is one of integer numbers 1 to 4 both inclusive. c4 is one of integer numbers 0 to 4 both inclusive. Each of f4 and m4 is one of integer numbers 1 to 3 both inclusive.

(10)

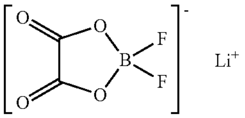


In Formula (10), X51 is one of Group 1 elements and Group 2 elements in the long-period periodic table. M51 is one of transition metals, Group 13 elements, Group 14 elements, and Group 15 elements in the long-period periodic table. Rf is one of a fluorinated alkyl group with carbon number from 1 to 10 both inclusive and a fluorinated aryl group with carbon number from 1 to 10 both inclusive. Y51 is one of —C(=O)—$(CR51_2)_{d5}$—C(=O)—, —$R52_2$C—$(CR51_2)_{d5}$—C(=O)—, —$R52_2$C—$(CR51_2)_{d5}$—$CR52_2$—, —$R52_2$C—$(CR51_2)_{d5}$—S(=O)$_2$—, —S(=O)$_2$—$(CR51_2)_{c5}$—S(=O)$_2$—, and —C(=O)—$(CR51_2)_{c5}$—S(=O)$_2$—. R51 is one of a hydrogen group, an alkyl group, a halogen group, and a halogenated alkyl group. R52 is one of a hydrogen group, an alkyl group, a halogen group, and a halogenated alkyl group, and one or more thereof are each a halogen group or a halogenated alkyl group. Each of a5, f5, and n5 is one of integer numbers 1 and 2. Each of b5, c5, and e5 is one of integer numbers 1 to 4 both inclusive. d5 is one of integer numbers 0 to 4 both inclusive. Each of g5 and m5 is one of integer numbers 1 to 3 both inclusive.

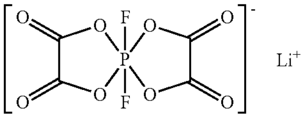
It is to be noted that Group 1 elements include H, Li, Na, K, Rb, Cs, and Fr. Group 2 elements include Be, Mg, Ca, Sr, Ba, and Ra. Group 13 elements include B, Al, Ga, In, and Tl. Group 14 elements include C, Si, Ge, Sn, and Pb. Group 15 elements include N, P, As, Sb, and Bi.

Examples of the compound represented by Formula (8) include compounds represented by Formula (8-1) to Formula (8-6). Examples of the compound represented by Formula (9) include compounds represented by Formula (9-1) to Formula (9-8). Examples of the compound represented by Formula (10) include a compound represented by Formula (10-1).

(8-1)

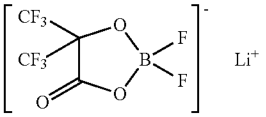


(8-2)

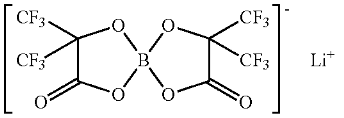


-continued

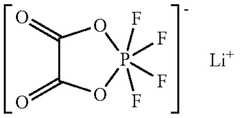
(8-3)



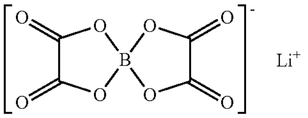
(8-4)



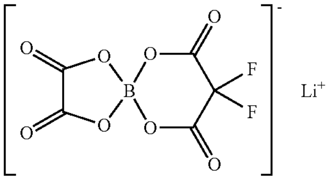
(8-5)



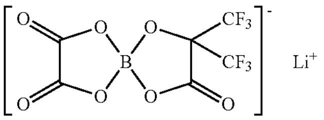
(8-6)



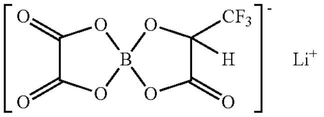
(9-1)



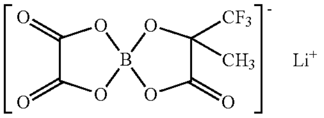
(9-2)



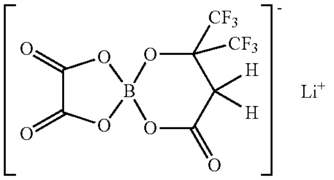
(9-3)



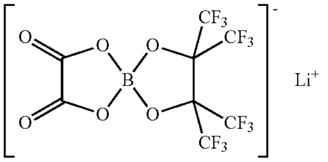
(9-4)



(9-5)

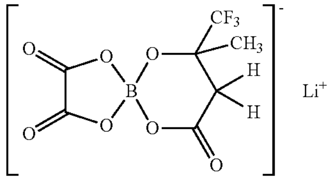


(9-6)

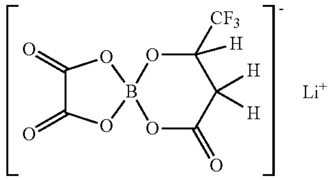


-continued

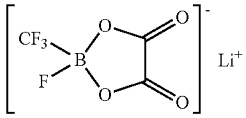
(9-7)



(9-8)



(10-1)

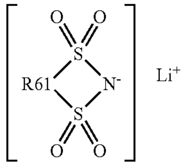


Further, the electrolyte salt preferably contains one or more of compounds represented by the following Formula (11) to the following Formula (13), since a higher effect is obtained thereby. It is to be noted that m and n may be the same value or values different from each other. The same is applied to p, q, and r. However, specific examples of the compounds represented by Formula (11) to Formula (13) are not limited to compounds described below.

$$LiN(C_mF_{2m+1}SO_2)(C_nF_{2n+1}SO_2) \quad (11)$$

In Formula (11), each of m and n is an integer number equal to or greater than 1.

(12)



In Formula (12), R61 is a straight-chain or branched perfluoro alkylene group with carbon number from 2 to 4 both inclusive.

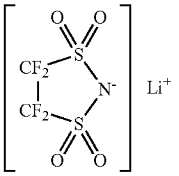
$$LiC(C_pF_{2p+1}SO_2)(C_qF_{2q+1}SO_2)(C_rF_{2r+1}SO_2) \quad (13)$$

In Formula (13), each of p, q, and r is an integer number equal to or greater than 1.

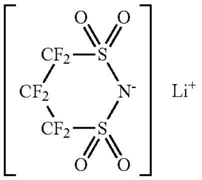
The compound represented by Formula (11) is a chain imide compound. Examples thereof include lithium bis(trifluoromethanesulfonyl)imide ($LiN(CF_3SO_2)_2$), lithium bis(pentafluoroethanesulfonyl)imide ($LiN(C_2F_5SO_2)_2$), lithium (trifluoromethanesulfonyl)(pentafluoroethanesulfonyl)imide ($LiN(CF_3SO_2)(C_2F_5SO_2)$), lithium(trifluoromethanesulfonyl)(heptafluoropropanesulfonyl)imide ($LiN(CF_3SO_2)(C_3F_7SO_2))_5$ and lithium (trifluoromethanesulfonyl)(nonafluorobutanesulfonyl)imide ($LiN(CF_3SO_2)(C_4F_9SO_2)$).

The compound represented by Formula (12) is a cyclic imide compound. Examples thereof include compounds represented by Formula (12-1) to Formula (12-4).

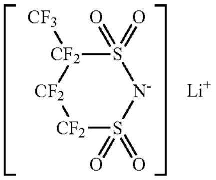
(12-1)



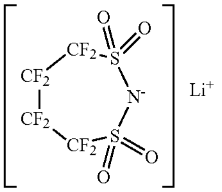
(12-2)



(12-3)



(12-4)



The compound represented by Formula (13) is a chain methyde compound. Examples thereof include lithium tris (trifluoromethanesulfonyl)methyde ($LiC(CF_3SO_2)_3$).

Although the content of the electrolyte salt is not particularly limited, in particular, the content thereof is preferably from 0.3 mol/kg to 3.0 mol/kg both inclusive with respect to the solvent, since high ion conductivity is obtained thereby.

[Operation of Secondary Battery]

In the secondary battery, for example, at the time of charge, lithium ions extracted from the cathode **21** are inserted in the anode **22** through the electrolytic solution. Further, at the time of discharge, lithium ions extracted from the anode **22** are inserted in the cathode **21** through the electrolytic solution.

In this case, the open circuit voltage in a fully-charged state per a pair of the cathode **21** and the anode **22** is preferably set to a value equal to or more than 4.3 V by adjusting amounts of the cathode active material and the anode active material. One reason for this is that, in this case, the extraction amount of lithium ions per unit mass is increased more compared to in a case where the open circuit voltage is less than 4.3 V even if the same type of anode active material is used for both cases, and therefore, high energy density is obtained. The foregoing "open circuit voltage in a fully-charged state" is an electric potential (battery voltage) of the cathode **21** in a fully-charged state, and refers to the so-called upper limit value of a charging voltage.

[Method of Manufacturing Secondary Battery]

The secondary battery is manufactured, for example, by the following procedure.

First, the cathode **21** is fabricated. A cathode active material is mixed with a cathode binder, a cathode electric conductor, and/or the like as necessary to prepare a cathode mixture. Subsequently, the cathode mixture is dispersed in an organic solvent or the like to obtain paste cathode mixture slurry. Subsequently, both surfaces of the cathode current collector **21**A are coated with the cathode mixture slurry, which is dried to form the cathode active material layer **21**B. In this case, the cathode active material layer **21**B may be formed only on a single surface of the cathode current collector **21**A. Subsequently, the cathode active material layer **21**B is compression-molded by using a roll pressing machine and/or the like while being heated as necessary. In this case, compression-molding may be repeated several times.

Further, the anode **22** is fabricated by a procedure similar to that of the cathode **21** described above. An anode active material is mixed with an anode binder, an anode electric conductor, and/or the like as necessary to prepare an anode mixture, which is subsequently dispersed in an organic solvent or the like to form paste anode mixture slurry. Subsequently, a single surface or both surfaces of the anode current collector **22**A are coated with the anode mixture slurry, which is dried to form the anode active material layer **22**B. Thereafter, the anode active material layer **22**B is compression-molded as necessary.

Further, after an electrolyte salt is dispersed in a solvent, an unsaturated cyclic ester carbonate is added thereto to prepare an electrolytic solution.

Finally, the secondary battery is assembled by using the cathode **21** and the anode **22**. The cathode lead **25** is attached to the cathode current collector **21**A by using a welding method and/or the like, and the anode lead **26** is attached to the anode current collector **22**A by using a welding method and/or the like. Subsequently, the heat-resistant layer **27** is formed on the surface of the separator **23** by using a coating method. Subsequently, the cathode **21** and the anode **22** are layered with the separator **23** on which the heat-resistant layer **27** is formed in between and are spirally wound, and thereby the spirally wound electrode body **20** is fabricated. Thereafter, the center pin **24** is inserted in the center of the spirally wound electrode body. Subsequently, the spirally wound electrode body **20** is sandwiched between the pair of insulating plates **12** and **13**, and is contained in the battery can **11**. In this case, the end tip of the cathode lead **25** is attached to the safety valve mechanism **15** by using a welding method and/or the like, and the end tip of the anode lead **26** is attached to the battery can **11** by using a welding method and/or the like. Subsequently, the electrolytic solution is injected into the battery can **11**, and the separator **23** is impregnated with the electrolytic solution. Subsequently, at the open end of the battery can **11**, the battery cover **14**, the safety valve mechanism **15**, and the PTC device **16** are fixed by being swaged with the gasket **17**.

[Function and Effect of Secondary Battery]

According to the cylindrical-type secondary battery, the heat-resistant layer **27** having a higher melting point or higher decomposition temperature than the melting point or the decomposition temperature of the separator **23** is provided at least in the opposed region R, and the electrolytic solution contains the unsaturated cyclic ester carbonate. In this case, as described above, conduction between the cathode **21** and the anode **22** is prevented even if the separator **23** is, for example, melted at the time of charge and discharge, differently from a case in which the melting point or the decomposition temperature of the heat-resistant layer **27** is equal to or less than the melting point or the decomposition temperature of the separator **23**. Further, the chemical stability of the electrolytic solution is improved. Thereby, even if the secondary battery is charged or stored, occurrence of short circuit is suppressed, and a decomposition reaction of the electrolytic solution is suppressed. Therefore, superior battery characteristics are obtainable.

In particular, in the case where the heat-resistant layer **27** contains a polymer compound such as polyamide or an oxide such as aluminum oxide, higher effects are obtainable.

Further, in the case where the content of the unsaturated cyclic ester carbonate in the electrolytic solution is from 0.01 wt % to 10 wt % both inclusive, higher effects are obtainable. Furthermore, in the case where the unsaturated cyclic ester carbonate is one of the compounds represented by Formula (1-1) to Formula (1-56), and in particular, is the compound represented by Formula (2) or the compound represented by Formula (3), higher effects are obtainable.

Further, in the case where the open circuit voltage in a fully-charged state per a pair of the cathode **21** and the anode **22** is equal to or more than 4.3 V, higher effects are obtainable while the foregoing advantage is secured.

[1-2. Modifications]

As described above, as long as the heat-resistant layer **27** is formed at least in the opposed region R, the formation range thereof is not particularly limited. Specifically, in FIG. **3**, the formation range of the heat-resistant layer **27** is extended toward the inner side and the outer side of the spirally wound body, the formation range of the heat-resistant layer **27** being beyond the formation range of the anode active material layer **22**B. On the other hand, for example, as illustrated in FIG. **4**, the formation range of the heat-resistant layer **27** may correspond with the formation range of the anode active material layer **22**B. Further, as illustrated in FIG. **5**, the formation range of the heat-resistant layer **27** may be narrower than the formation range of the anode active material layer **22**B, and more specifically, the heat-resistant layer **27** may be provided only in the opposed region R. In either case, similar effects are obtainable.

Further, the heat-resistant layer **27** is not necessarily provided on both surfaces of the separator **23**. Specifically, for example, as illustrated in FIG. **6**, the heat-resistant layer **27** may be provided only on one surface (surface on the side opposed to the anode **22**) of the separator **23**. Alternatively, as illustrated in FIG. **7**, the heat-resistant layer **27** may be provided only on the other surface (surface on the side opposed to the cathode **21**) of the separator **23**. In either case, similar effects are obtainable. In particular, in the former case, even if the secondary battery is stored under strict conditions such as high temperature and a high voltage, a movement path (diffusion path) of lithium ions is allowed to be secured while a reaction between the anode **22** and the separator **23** is inhibited. In this case, a decomposed matter and/or the like is allowed to be prevented from being deposited on the surface of the anode **22**. On the other hand, in the latter case, even if the secondary battery is stored under strict conditions such as high temperature and a high voltage, a reaction between the cathode **21** and the separator **23** is allowed to be inhibited, and lowered intensity of the separator **23** caused by oxidation is allowed to be prevented.

Further, as long as the heat-resistant layer **27** is formed at least in the opposed region R between the cathode **21** and the anode **22**, the formation location thereof is not particularly limited. Specifically, in FIG. **3**, the heat-resistant layer **27** is provided on the separator **23**. On the other hand, for example, as illustrated in FIG. **8**, the heat-resistant layer **27** may be provided on the cathode **21** and the anode **22** so that the heat-resistant layer **27** is located between the cathode **21** and the separator **23**, and between the anode **22** and the separator **23**. Alternatively, as illustrated in FIG. **9**, the heat-resistant layer **27** may be provided only on the anode

22. Alternatively, as illustrated in FIG. **10**, the heat-resistant layer **27** may be provided only on the cathode **21**. In these cases, similar effects are obtainable. It is to be noted that, in the case where the heat-resistant layer **27** is provided on the cathode **21** or on the anode **22**, the modifications illustrated in FIG. **4** and FIG. **5** may be applied as appropriate.

It goes without saying that two or more of the examples illustrated in FIG. **3** to FIG. **10** may be combined. As an example, as illustrated in FIG. **11**, the heat-resistant layer **27** may be provided on all of the cathode **21**, the anode **22**, and the separator **23**. In this case, short circuit is further prevented, and therefore, higher effects are obtainable.

[1-2. Laminated Film Type]

FIG. **12** illustrates an exploded perspective configuration of another secondary battery according to the embodiment of the present application. FIG. **13** illustrates an enlarged cross-section taken along a line XIII-XIII of a spirally wound electrode body **30** illustrated in FIG. **12**. FIG. **14** illustrates enlarged part of the spirally wound electrode body **30** illustrated in FIG. **13**. In the following description, the elements of the cylindrical-type secondary battery described above will be used as necessary.

[Whole Configuration of Secondary Battery]

The secondary battery described here is, for example, a so-called laminated-film-type lithium ion secondary battery as illustrated in FIG. **12** and FIG. **13**. In the secondary battery, the spirally wound electrode body **30** is contained in a film-like outer package member **40**. In the spirally wound electrode body **30**, a cathode **33** and an anode **34** are layered with a separator **35** and an electrolyte layer **36** in between and are spirally wound. A cathode lead **31** is attached to the cathode **33**, and an anode lead **32** is attached to the anode **34**. The outermost periphery of the spirally wound electrode body **30** is protected by a protective tape **37**.

The cathode lead **31** and the anode lead **32** are, for example, led out from inside to outside of the outer package member **40** in the same direction. The cathode lead **31** is made of, for example, a conductive material such as aluminum, and the anode lead **32** is made of, for example, a conducive material such as copper, nickel, and stainless steel. These conductive materials are in the shape of, for example, a thin plate or mesh.

The outer package member **40** is a laminated film in which, for example, a fusion bonding layer, a metal layer, and a surface protective layer are laminated in this order. In the laminated film, for example, the respective outer edges of the fusion bonding layers of two films are bonded to each other by fusion bonding, so that the fusion bonding layers and the spirally wound electrode body **30** are opposed to each other. The two films may be attached to each other by an adhesive, or the like. Examples of the fusion bonding layer include a film made of polyethylene, polypropylene, or the like. Examples of the metal layer include an aluminum foil. Examples of the surface protective layer include a film made of nylon, polyethylene terephthalate, or the like.

In particular, as the outer package member **40**, an aluminum laminated film in which a polyethylene film, an aluminum foil, and a nylon film are laminated in this order is preferable. However, the outer package member **40** may be made of a laminated film having other laminated structure, a polymer film such as polypropylene, or a metal film.

An adhesive film **41** to protect from outside air intrusion is inserted between the outer package member **40** and the cathode lead **31** and between the outer package member **40** and the anode lead **32**. The adhesive film **41** is made of a material having adhesion characteristics with respect to the cathode lead **31** and the anode lead **32**. Examples of the material having adhesion characteristics include a polyolefin resin such as polyethylene, polypropylene, modified polyethylene, and modified polypropylene.

The cathode **33** has, for example, a cathode active material layer **33**B on a single surface or both surfaces of a cathode current collector **33**A. The anode **34** has, for example, an anode active material layer **34**B on a single surface or both surfaces of an anode current collector **34**A. The configurations of the cathode current collector **33**A, the cathode active material layer **33**B, the anode current collector **34**A, and the anode active material layer **34**B are similar to the configurations of the cathode current collector **21**A, the cathode active material layer **21**B, the anode current collector **22**A, and the anode active material layer **22**B, respectively. Further, the configuration of the separator **35** is similar to the configuration of the separator **23**.

In the electrolyte layer **36**, an electrolytic solution is held by a polymer compound. The electrolyte layer **36** is a so-called gel electrolyte, since thereby, high ion conductivity (for example, 1 mS/cm or more at room temperature) is obtained and liquid leakage of the electrolytic solution is prevented. The electrolyte layer **36** may contain other material such as an additive as necessary.

Examples of the polymer compound include one or more of polyacrylonitrile, polyvinylidene fluoride, polytetrafluoroethylene, polyhexafluoropropylene, polyethylene oxide, polypropylene oxide, polyphosphazene, polysiloxane, polyvinyl fluoride, polyvinyl acetate, polyvinyl alcohol, polymethacrylic acid methyl, polyacrylic acid, polymethacrylic acid, styrene-butadiene rubber, nitrile-butadiene rubber, polystyrene, polycarbonate, and a copolymer of vinylidene fluoride and hexafluoro propylene. In particular, polyvinylidene fluoride or the copolymer of vinylidene fluoride and hexafluoro propylene is preferable, and polyvinylidene fluoride is more preferable, since such a polymer compound is electrochemically stable.

The composition of the electrolytic solution is similar to the composition of the electrolytic solution of the cylindrical-type secondary battery. The electrolytic solution contains the unsaturated cyclic ester carbonate. However, in the electrolyte layer **36** as a gel electrolyte, the solvent of the electrolytic solution refers to a wide concept including not only a liquid solvent but also a material having ion conductivity capable of dissociating the electrolyte salt. Therefore, in the case where a polymer compound having ion conductivity is used, the polymer compound is also included in the solvent.

It is to be noted that the electrolytic solution may be used as it is instead of the gel electrolyte layer **36**. In this case, the separator **35** is impregnated with the electrolytic solution.

In the secondary battery, for example, as illustrated in FIG. **14**, a heat-resistant layer **38** is provided at least in an opposed region in which the cathode active material layer **33**B and the anode active material layer **34**B are opposed to each other between the cathode **33** and the anode **34**. The heat-resistant layer **38** contains a material (heat-resistant material) having a higher melting point or higher decomposition temperature than a melting point or decomposition temperature of the separator **35**. In this case, for example, the heat-resistant layer **38** is provided on both surfaces of the separator **35**. Thereby, the heat-resistant layer **38** is located between the cathode **33** and the separator **35** and between the anode **34** and the separator **35**. Further, the electrolytic solution of the electrolyte layer **36** contains the unsaturated cyclic ester carbonate. Details of the heat-resistant layer **38** and the unsaturated cyclic ester carbonate are similar to the heat-resistant layer **27** and the unsaturated cyclic ester carbonate of the cylindrical-type secondary battery, and therefore, descriptions thereof will be omitted. It is to be noted that in FIG. **13**, illustration of the heat-resistant layer **38** is omitted.

[Operation of Secondary Battery]

In the secondary battery, for example, at the time of charge, lithium ions extracted from the cathode **33** are inserted in the anode **34** through the electrolyte layer **36**. On the other hand, at the time of discharge, lithium ions extracted from the anode **34** are inserted in the cathode **33** through the electrolyte layer **36**. In this case, although the open circuit voltage in a fully-charged state per a pair of the cathode **33** and the anode **34** is not particularly limited, the open circuit voltage is preferably equal to or more than 4.3 V to obtain high energy density as in the cylindrical-type secondary battery.

[Method of Manufacturing Secondary Battery]

The secondary battery including the gel electrolyte layer **36** is manufactured, for example, by the following three types of procedures.

In the first procedure, the cathode **33** and the anode **34** are fabricated by a fabrication procedure similar to that of the cathode **21** and the anode **22**. In forming the cathode **33**, the cathode active material layer **33**B is formed on a single surface or both surfaces of the cathode current collector **33**A. In forming the anode **34**, the anode active material layer **34**B is formed on a single surface or both surfaces of the anode current collector **34**A. Subsequently, a precursor solution including an electrolytic solution containing an unsaturated cyclic ester carbonate, a polymer compound, and a solvent such as an organic solvent is prepared. Thereafter, the cathode **33** and the anode **34** are coated with the precursor solution to form the gel electrolyte layer **36**. Subsequently, the cathode lead **31** is attached to the cathode current collector **33**A by using a welding method and/or the like and the anode lead **32** is attached to the anode current collector **34**A by using a welding method and/or the like. Subsequently, the heat-resistant layer **38** is formed on both surfaces of the separator **35**. Subsequently, the cathode **33** and the anode **34** are layered with the separator **35** on which the heat-resistant layer **38** is formed in between and are spirally wound to fabricate the spirally wound electrode body **30**. Thereafter, the protective tape **37** is adhered to the outermost periphery thereof. Subsequently, after the spirally wound electrode body **30** is sandwiched between two pieces of film-like outer package members **40**, the outer edges of the outer package members **40** are bonded by using a thermal fusion bonding method and/or the like. Thereby, the spirally wound electrode body **30** is enclosed into the outer package members **40**. In this case, the adhesive films **41** are inserted between the cathode lead **31** and the outer package member **40** and between the anode lead **32** and the outer package member **40**.

In the second procedure, the cathode lead **31** is attached to the cathode **33**, and the anode lead **32** is attached to the anode **34**. Subsequently, the cathode **33** and the anode **34** are layered with the separator **35** in between and are spirally wound to fabricate a spirally wound body as a precursor of the spirally wound electrode body **30**. Thereafter, the protective tape **37** is adhered to the outermost periphery thereof. Subsequently, after the spirally wound body is sandwiched between two pieces of the film-like outer package members **40**, the outermost peripheries except for one side are bonded by using a thermal fusion bonding method and/or the like to obtain a pouched state, and the spirally wound body is contained in the pouch-like outer package member **40**. Subsequently, a composition for electrolyte containing an electrolytic solution, a monomer as a raw material for the polymer compound, a polymerization initiator, and other materials such as a polymerization inhibitor as necessary is prepared, which is injected into the pouch-like outer package member **40**. Thereafter, the outer package member **40** is hermetically sealed by using a thermal fusion bonding method and/or the like. Subsequently, the monomer is thermally polymerized, and thereby, a polymer compound is formed. Accordingly, the gel electrolyte layer **36** is formed.

In the third procedure, the spirally wound body is fabricated and contained in the pouch-like outer package member **40** in a manner similar to that of the foregoing second procedure, except that the separator **35** with both surfaces coated with a polymer compound is used. Examples of the polymer compound with which the separator **35** is coated include a polymer (a homopolymer, a copolymer, or a multicomponent copolymer) containing vinylidene fluoride as a component. Specific examples thereof include polyvinylidene fluoride, a binary copolymer containing vinylidene fluoride and hexafluoro propylene as components, and a ternary copolymer containing vinylidene fluoride, hexafluoro propylene, and chlorotrifluoroethylene as components. In addition to the polymer containing vinylidene fluoride as a component, other one or more polymer compounds may be used. Subsequently, an electrolytic solution is prepared and injected into the outer package member **40**. Thereafter, the opening of the outer package member **40** is hermetically sealed by using a thermal fusion bonding method and/or the like. Subsequently, the resultant is heated while a weight is applied to the outer package member **40**, and the separator **35** is adhered to the cathode **33** and the anode **34** with the polymer compound in between. Thereby, the polymer compound is impregnated with the electrolytic solution, and accordingly, the polymer compound is gelated to form the electrolyte layer **36**.

In the third procedure, swollenness of the secondary battery is suppressed more than in the first procedure. Further, in the third procedure, the monomer as a raw material of the polymer compound, the solvent, and the like are less likely to be left in the electrolyte layer **36** compared to in the second procedure. Therefore, the formation step of the polymer compound is favorably controlled. Therefore, sufficient adhesion characteristics are obtained between the cathode **33**, the anode **34**, and the separator **35**, and the electrolyte layer **36**.

[Function and Effect of Secondary Battery]

According to the laminated-film-type secondary battery, the heat-resistant layer **38** having a higher melting point or higher decomposition temperature than the melting point or the decomposition temperature of the separator **35** is provided on the separator **35** at least in the opposed region in which the cathode active material layer **33**B and the anode active material layer **34**B are opposed to each other. Further, the electrolytic solution of the electrolyte layer **36** contains the unsaturated cyclic ester carbonate. Therefore, for a reason similar to that of the cylindrical-type secondary battery, superior battery characteristics are obtainable. Other functions, other effects, and modifications thereof are similar to those of the cylindrical-type secondary battery.

[2. Applications of Secondary Battery]

Next, a description will be given of application examples of the foregoing secondary battery.

Applications of the secondary battery are not particularly limited as long as the secondary battery is used for a machine, a device, an instrument, an apparatus, a system (collective entity of a plurality of devices and the like), or the like that is allowed to use the secondary battery as a driving electric power source, an electric power storage source for electric power storage, or the like. In the case where the secondary battery is used as an electric power source, the secondary battery may be used as a main electric power source (electric power source used preferentially), or an auxiliary electric power source (electric power source used instead of a main electric power source or used being switched from the main electric power source). In the latter case, the main electric power source type is not limited to the secondary battery.

Examples of applications of the secondary battery include electronic apparatuses (including portable electronic apparatuses) such as a video camcorder, a digital still camera, a mobile phone, a notebook personal computer, a cordless phone, a headphone stereo, a portable radio, a portable television, and a personal digital assistant. Further examples thereof include a mobile lifestyle electric appliance such as an electric shaver; a memory device such as a backup electric power source and a memory card; an electric power tool such as an electric drill and an electric saw; a battery pack used as an electric power source of a notebook personal computer or the like; a medical electronic apparatus such as a pacemaker and a hearing aid; an electric vehicle such as an electric automobile (including a hybrid automobile); and an electric power storage system such as a home battery system for storing electric power for emergency or the like. It goes without saying that an application other than the foregoing applications may be adopted.

In particular, the secondary battery is effectively applicable to the battery pack, the electric vehicle, the electric power storage system, the electric power tool, the electronic apparatus, or the like. In these applications, since superior battery characteristics are demanded, performance is effectively improved by using the secondary battery according to the embodiment of the present application. It is to be noted that the battery pack is an electric power source using a secondary battery, and is a so-called assembled battery or the like. The electric vehicle is a vehicle that works (runs) by using a secondary battery as a driving electric power source. As described above, an automobile (such as a hybrid automobile) including a drive source other than a secondary battery may be included. The electric power storage system is a system using a secondary battery as an electric power storage source. For example, in a home electric power storage system, electric power is stored in the secondary battery as an electric power storage source, and the electric power is consumed as necessary. Thereby, home electric products and the like become usable. The electric power tool is a tool in which a movable section (such as a drill) is moved by using a secondary battery as a driving electric power source. The electronic apparatus is an apparatus executing various functions by using a secondary battery as a driving electric power source (electric power supply source).

A description will be specifically given of some application examples of the secondary battery. The configurations of the respective application examples explained below are merely examples, and may be changed as appropriate.

[2-1. Battery Pack]

FIG. **15** illustrates a block configuration of a battery pack. For example, as illustrated in FIG. **15**, the battery pack includes a control section **61**, an electric power source **62**, a switch section **63**, a current measurement section **64**, a temperature detection section **65**, a voltage detection section **66**, a switch control section **67**, a memory **68**, a temperature detection device **69**, a current detection resistance **70**, a cathode terminal **71**, and an anode terminal **72** in a housing **60** made of a plastic material and/or the like.

The control section **61** controls operation of the whole battery pack (including a used state of the electric power source **62**), and includes, for example, a central processing unit (CPU) and/or the like. The electric power source **62** includes one or more secondary batteries (not illustrated). The electric power source **62** is, for example, an assembled battery including two or more secondary batteries. Connection type thereof may be a series-connected type, may be a parallel-connected type, or a mixed type thereof. As an example, the electric power source **62** includes six secondary batteries connected in a manner of dual-parallel and three-series.

The switch section **63** switches the used state of the electric power source **62** (whether or not the electric power source **62** is connectable to an external device) according to an instruction of the control section **61**. The switch section **63** includes, for example, a charge control switch, a discharge control switch, a charging diode, a discharging diode, and the like (not illustrated). The charge control switch and the discharge control switch are each, for example, a semiconductor switch such as a field-effect transistor (MOSFET) using a metal oxide semiconductor.

The current measurement section **64** measures a current by using the current detection resistance **70**, and outputs the measurement result to the control section **61**. The temperature detection section **65** measures temperature by using the temperature detection device **69**, and outputs the measurement result to the control section **61**. The temperature measurement result is used for, for example, a case in which the control section **61** controls charge and discharge at the time of abnormal heat generation or a case in which the control section **61** performs a correction processing at the time of calculating a remaining capacity. The voltage detection section **66** measures a voltage of the secondary battery in the electric power source **62**, performs analog-to-digital conversion (A/D conversion) on the measured voltage, and supplies the resultant to the control section **61**.

The switch control section **67** controls operations of the switch section **63** according to signals inputted from the current measurement section **64** and the voltage measurement section **66**.

The switch control section **67** executes control so that a charging current is prevented from flowing in a current path of the electric power source **62** by disconnecting the switch section **63** (charge control switch) in the case where, for example, a battery voltage reaches an overcharge detection voltage. Thereby, in the electric power source **62**, only discharge is allowed to be performed through the discharging diode. It is to be noted that, for example, in the case where a large current flows at the time of charge, the switch control section **67** blocks the charging current.

Further, the switch control section **67** executes control so that a discharging current is prevented from flowing in the current path of the electric power source **62** by disconnecting the switch section **63** (discharge control switch) in the case where, for example, a battery voltage reaches an overdischarge detection voltage. Thereby, in the electric power source **62**, only charge is allowed to be performed through the charging diode. For example, in the case where a large current flows at the time of discharge, the switch control section **67** blocks the discharging current.

It is to be noted that, in the secondary battery, for example, the overcharge detection voltage is 4.2 V±0.05 V, and the over-discharge detection voltage is 2.4 V±0.1V.

The memory **68** is, for example, an EEPROM as a nonvolatile memory or the like. The memory **68** stores, for example, numerical values calculated by the control section **61** and information of the secondary battery measured in a manufacturing step (such as an internal resistance in the initial state). It is to be noted that, in the case where the memory **68** stores a full charge capacity of the secondary battery, the control section **61** is allowed to comprehend information such as a remaining capacity.

The temperature detection device **69** measures temperature of the electric power source **62**, and outputs the measurement result to the control section **61**. The temperature detection device **69** is, for example, a thermistor or the like.

The cathode terminal **71** and the anode terminal **72** are terminals connected to an external device (such as a notebook personal computer) driven by using the battery pack or an external device (such as a battery charger) used for charging the battery pack. The electric power source **62** is charged and discharged through the cathode terminal **71** and the anode terminal **72**.

[2-2. Electric Vehicle]

FIG. **16** illustrates a block configuration of a hybrid automobile as an example of electric vehicles. For example, as illustrated in FIG. **16**, the electric vehicle includes a control section **74**, an engine **75**, an electric power source **76**, a driving motor **77**, a differential **78**, an electric generator **79**, a transmission **80**, a clutch **81**, inverters **82** and **83**, and various sensors **84** in a housing **73** made of metal. In addition thereto, the electric vehicle includes, for example, a front drive shaft **85** and a front tire **86** that are connected to the differential **78** and the transmission **80**, a rear drive shaft **87**, and a rear tire **88**.

The electric vehicle is runnable by using one of the engine **75** and the motor **77** as a drive source. The engine **75** is a main power source, and is, for example, a petrol engine. In the case where the engine **75** is used as a power source, drive power (torque) of the engine **75** is transferred to the front tire **86** or the rear tire **88** through the differential **78**, the transmission **80**, and the clutch **81** as drive sections, for example. The torque of the engine **75** is also transferred to the electric generator **79**. Due to the torque, the electric generator **79** generates alternating-current electric power. The alternating-current electric power is converted into direct-current electric power through the inverter **83**, and the converted power is stored in the electric power source **76**. On the other hand, in the case where the motor **77** as a conversion section is used as a power source, electric power (direct-current electric power) supplied from the electric power source **76** is converted into alternating-current electric power through the inverter **82**. The motor **77** is driven by the alternating-current electric power. Drive power (torque) obtained by converting the electric power by the motor **77** is transferred to the front tire **86** or the rear tire **88** through the differential **78**, the transmission **80**, and the clutch **81** as the drive sections, for example.

It is to be noted that, alternatively, the following mechanism may be adopted. In the mechanism, in the case where speed of the electric vehicle is reduced by an unillustrated brake mechanism, the resistance at the time of speed reduction is transferred to the motor **77** as torque, and the motor **77** generates alternating-current electric power by the torque. It is preferable that the alternating-current electric power be converted to direct-current electric power through the inverter **82**, and the direct-current regenerative electric power be stored in the electric power source **76**.

The control section **74** controls operations of the whole electric vehicle, and, for example, includes a CPU and/or the like. The electric power source **76** includes one or more secondary batteries (not illustrated). Alternatively, the electric power source **76** may be connected to an external electric power source, and electric power may be stored by receiving the electric power from the external electric power source. The various sensors **84** are used, for example, for controlling the number of revolutions of the engine **75** or for controlling opening level (throttle opening level) of an unillustrated throttle valve. The various sensors **84** include, for example, a speed sensor, an acceleration sensor, an engine frequency sensor, and/or the like.

The description has been given of the hybrid automobile as an electric vehicle. However, examples of the electric vehicles may include a vehicle (electric automobile) working by using only the electric power source **76** and the motor **77** without using the engine **75**.

[2-3. Electric Power Storage System]

FIG. **17** illustrates a block configuration of an electric power storage system. For example, as illustrated in FIG. **17**, the electric power storage system includes a control section **90**, an electric power source **91**, a smart meter **92**, and a power hub **93** inside a house **89** such as a general residence and a commercial building.

In this case, the electric power source **91** is connected to, for example, an electric device **94** arranged inside the house **89**, and is connectable to an electric vehicle **96** parked outside the house **89**. Further, for example, the electric power source **91** is connected to a private power generator **95** arranged inside the house **89** through the power hub **93**, and is connectable to an external concentrating electric power system **97** thorough the smart meter **92** and the power hub **93**.

It is to be noted that the electric device **94** includes, for example, one or more home electric appliances such as a refrigerator, an air conditioner, a television, and a water heater. The private power generator **95** is, for example, one or more of a solar power generator, a wind-power generator, and the like. The electric vehicle **96** is, for example, one or more of an electric automobile, an electric motorcycle, a hybrid automobile, and the like. The concentrating electric power system **97** is, for example, one or more of a thermal power plant, an atomic power plant, a hydraulic power plant, a wind-power plant, and the like.

The control section **90** controls operations of the whole electric power storage system (including a used state of the electric power source **91**), and, for example, includes a CPU and/or the like. The electric power source **91** includes one or more secondary batteries (not illustrated). The smart meter **92** is, for example, an electric power meter compatible with a network arranged in the house **89** demanding electric power, and is communicable with an electric power supplier. Accordingly, for example, while the smart meter **92** communicates with outside as necessary, the smart meter **92** controls the balance between supply and demand in the house **89** and allows effective and stable energy supply.

In the electric power storage system, for example, electric power is stored in the electric power source **91** from the concentrating electric power system **97** as an external electric power source through the smart meter **92** and the power hub **93**, and electric power is stored in the electric power source **91** from the private power generator **95** as an independent electric power source through the power hub **93**. As necessary, the electric power stored in the electric power source **91** is supplied to the electric device **94** or to the electric vehicle **96** according to an instruction of the control section **90**. Therefore, the electric device **94** becomes operable, and the electric vehicle **96** becomes chargeable. That is, the electric power storage system is a system capable of storing and supplying electric power in the house **89** by using the electric power source **91**.

The electric power stored in the electric power source **91** is arbitrarily usable. Therefore, for example, electric power is allowed to be stored in the electric power source **91** from the concentrating electric power system **97** in the middle of the night when an electric rate is inexpensive, and the electric power stored in the electric power source **91** is allowed to be used during daytime hours when an electric rate is expensive.

The foregoing electric power storage system may be arranged for each household (family unit), or may be arranged for a plurality of households (family units).

[2-4. Electric Power Tool]

FIG. **18** illustrates a block configuration of an electric power tool. For example, as illustrated in FIG. **18**, the electric power tool is an electric drill, and includes a control section **99** and an electric power source **100** in a tool body **98** made of a plastic material and/or the like. For example, a drill section **101** as a movable section is attached to the tool body **98** in an operable (rotatable) manner.

The control section **99** controls operations of the whole electric power tool (including a used state of the electric power source **100**), and includes, for example, a CPU and/or the like. The electric power source **100** includes one or more secondary batteries (not illustrated). The control section **99** executes control so that electric power is supplied from the electric power source **100** to the drill section **101** as necessary according to operation of an unillustrated operation switch to operate the drill section **101**.

EXAMPLES

Specific Examples according to the embodiment of the present application will be described in detail.

Examples 1-1 to 1-32

The cylindrical-type lithium ion secondary battery illustrated in FIG. **1** and FIG. **2** was fabricated by the following procedure.

In fabricating the cathode **21**, first, lithium carbonate (Li_2CO_3) and cobalt carbonate ($CoCO_3$) were mixed at a molar ratio of Li_2CO_3:$CoCO_3$=0.5:1. Subsequently, the mixture was fired in the air (900 deg C. for 5 hours). Thereby, lithium-cobalt composite oxide ($LiCoO_2$) was obtained. Subsequently, 94 parts by mass of a cathode active material ($LiCoO_2$), 3 parts by mass of a cathode binder (polyvinylidene fluoride: PVDF), and 3 parts by mass of a cathode electric conductor (graphite) were mixed to obtain a cathode mixture. Subsequently, the cathode mixture was dispersed in an organic solvent (N-methyl-2-pyrrolidone: NMP) to obtain paste cathode mixture slurry. Subsequently, both surfaces of the cathode current collector **21**A in the shape of a strip (aluminum foil being 10 μm thick) were coated with the cathode mixture slurry uniformly by using a coating device, which was dried to form the cathode active material layer **21**B. Finally, the cathode active material layer **21**B was compression-molded by using a roll pressing machine.

In fabricating the anode **22**, first, 97 parts by mass of an anode active material (artificial graphite) and 3 parts by mass of an anode binder (PVDF) were mixed to obtain an anode mixture. Subsequently, the anode mixture was dispersed in an organic solvent (NMP) to obtain paste anode mixture slurry. Subsequently, both surfaces of the anode current collector **22**A in the shape of a strip (electrolytic copper foil being 10 μm thick) were coated with the anode mixture slurry uniformly by using a coating device, which was dried to form the anode active material layer **22**B. Finally, the anode active material layer **22**B was compression-molded by using a roll pressing machine.

In preparing the separator **23** provided with the heat-resistant layer **27**, as illustrated in FIG. **3**, the heat-resistant layer **27** was formed on both surfaces of the separator **23**. As illustrated in Table 1 and Table 2, a formation material of the heat-resistant layer **27** is a polymer material or an oxide having a higher melting point or higher decomposition temperature than the melting point or the decomposition temperature of the separator **23**. Specifically, the polymer compound is a para-type aromatic polyamide (PA1) represented by Formula (30-1) and a meta-type aromatic polyamide (PA2) represented by Formula (30-2). The oxide is aluminum oxide (Al_2O_3), titanium oxide (TiO_2), or silicon oxide (SiO_2). For comparison, polyethylene (PE) as a polymer material having a lower melting point or lower decomposition temperature than the melting point or the decomposition temperature of the separator **23** was used as well. The thickness of the heat-resistant layer **27** was 2 μm, and the density was 0.3 mg/cm^2. In the case where the polymer compound was used, after the polymer compound was dissolved in an organic solvent (NMP), the separator **23** was coated with the resultant solution thereof, and the resultant was dried. In the case where the oxide was used, after the oxide and a retaining polymer compound (PVDF) were mixed at a weight ratio of oxide:retaining polymer compound=20:1, the resultant mixture was dispersed in an organic solvent (NMP). Subsequently, after the separator **23** (a polyethylene microporous film having a fine pore diameter of 17.9 nm) was coated with the resultant dispersive solution by using a desktop coater, the resultant was bathed and phase-separated, and was subsequently dried in the hot air. As specifications of the oxide, the central particle diameter (X) was 0.3 μm, and the specific surface area (Y) was 13 m^2/g.

A fabrication procedure of the polyethylene microporous film as the separator **23** was as follows. First, a polyethylene resin and a plasticizer (liquid paraffin) were melted and kneaded by using a biaxial extruder to prepare a polyethylene solution. Subsequently, while the polyethylene solution was extruded from a T-die attached to the end of the biaxial extruder at predetermined temperature, the extruded portion was wound around a cooling roll, and thereby a gel sheet was formed. Subsequently, the gel sheet was biaxially-stretched to obtain a thin film. Finally, the thin film was washed with hexane to extract and remove remaining liquid paraffin. Thereafter, the resultant was dried and subjected to heat treatment to obtain a microporous thin film. Thereby, the polyethylene microporous film was obtained.

In preparing an electrolytic solution, an electrolyte salt ($LiPF_6$) was dissolved in a solvent (ethylene carbonate (EC) and dimethyl carbonate (DMC)). Thereafter, as illustrated in Table 1 and Table 2, as necessary, an unsaturated cyclic ester carbonate was added thereto. In this case, the composition of the solvent was EC:DMC=50:50 at a weight ratio, and the content of the electrolyte salt with respect to the solvent was 1 mol/kg.

In assembling the secondary battery, first, the cathode lead **25** made of aluminum was welded to the cathode current collector **21**A, and the anode lead **26** made of nickel was welded to the anode current collector **22**A. Subsequently, the cathode **21** and the anode **22** were layered with the separator **23** in which the heat-resistant layer **27** was formed in between and were spirally wound. Thereafter, the winding end section was fixed by using an adhesive tape to fabricate the spirally wound electrode body **20**. Subsequently, the center pin **24** was inserted in the center of the spirally wound electrode body **20**. Subsequently, while the spirally wound electrode body **20** was sandwiched between the pair of insulating plates **12** and **13**, the spirally wound electrode body **20** was contained in the battery can **11** made of iron and plated with nickel. In this case, one end of the cathode lead **25** was welded to the safety valve mechanism **15**, and one end of the anode lead **26** was welded to the battery can **11**. Subsequently, the electrolytic solution was injected into the battery can **11** by a depressurization method, and the separator **23** was impregnated with the electrolytic solution. Finally, at the open end of the battery can **11**, the battery cover **14**, the safety valve mechanism **15**, and the PTC device **16** were fixed by being swaged with the gasket **17**. The cylindrical-type secondary battery was thereby completed. In fabricating the secondary battery, lithium metal was prevented from being precipitated on the anode **22** at the time of full charge by adjusting the thickness of the cathode active material layer **21**B.

Battery characteristics (cycle characteristics and continuous charge characteristics) of the secondary battery were examined. Results illustrated in Table 1 and Table 2 were obtained.

In examining the cycle characteristics, one cycle of charge and discharge was performed on the secondary battery in the ambient temperature environment (23 deg C.) to stabilize the battery state. Thereafter, another one cycle of charge and discharge was performed on the secondary battery in the same environment, and a discharge capacity was measured. Subsequently, the secondary battery was repeatedly charged and discharged until the total number of cycles reached 100 in high temperature environment (60 deg C.), and a discharge capacity was measured. From these results, cycle retention ratio (%)=(discharge capacity at the 100th cycle/discharge capacity at the second cycle)×100 was calculated. At the time of charge, charge was performed at a current of 1 C until the voltage reached the upper limit voltage of 4.2 V, and further charge was performed at a constant voltage until the total time from starting charge reached 3 hours. At the time of discharge, discharge was performed at a current of 1 C until the voltage reached the final voltage of 3 V. "1 C" is a current value at which the battery capacity (theoretical capacity) is fully discharged in 1 hour.

In examining the continuous charge characteristics, one cycle of charge and discharge was performed on the secondary battery in the ambient temperature environment (23 deg C.) to stabilize the battery state. Thereafter, another one cycle of charge and discharge was performed on the secondary battery in the same environment, and a discharge capacity was measured. Subsequently, the secondary battery was charged at a constant current (current: 0.5 C) until the secondary battery became in a fully-charged state (the upper limit voltage of the charging voltage: 4.2 V) in high temperature environment (60 deg C.). Thereafter, the constant current charge was switched to constant voltage charge, and continuous charge (600 hours) was performed on the secondary battery, on which discharge was performed to measure a discharge capacity. From these results, continuous charge retention ratio (%)=(discharge capacity after continuous charge/discharge capacity before continuous charge)×100 was calculated. "0.5 C" is a current value at which the battery capacity is fully discharged in 2 hours. Charge and discharge conditions other than the foregoing conditions are similar to those in the case of examining the cycle characteristics. In this case, not only the foregoing continuous charge retention ratio was calculated, but also a leak current (mA) at the time of continuous charge was measured.

TABLE 1

Charging voltage (upper limit value): 4.2 V

	Heat-resistant layer		Electrolytic solution		Unsaturated cyclic ester carbonate		Cycle retention	Continuous charge retention	Leak
Example	Formation location	Type	Electrolyte salt	Solvent	Type	Content (wt %)	ratio (%)	ratio (%)	current (mA)
1-1	Separator	PA1	$LiPF_6$	EC + DMC	Formula (1-1)	0.01	25	55	6
1-2						0.1	40	60	4
1-3						0.5	52	68	2.3
1-4						1	61	76	1
1-5						2	73	82	0.6
1-6						5	72	82	0.6
1-7						10	68	80	0.6
1-8		PA2	$LiPF_6$	EC + DMC	Formula (1-1)	2	66	78	0.5
1-9		PVDF + Al_2O_3	$LiPF_6$	EC + DMC	Formula (1-1)	0.01	28	63	5
1-10						0.1	50	68	3
1-11						0.5	57	75	1.4
1-12						1	64	78	0.6
1-13						2	74	84	0.5
1-14						5	73	84	0.5
1-15						10	70	80	0.5
1-16		PVDF + TiO_2	$LiPF_6$	EC + DMC	Formula (1-1)	2	67	80	0.7
1-17		PVDF + SiO_2	$LiPF_6$	EC + DMC	Formula (1-1)	2	67	80	0.7

TABLE 2

Charging voltage (upper limit value): 4.2 V

	Heat-resistant layer		Electrolytic solution				Cycle retention ratio (%)	Continuous charge retention ratio (%)	Leak current (mA)
					Unsaturated cyclic ester carbonate				
Example	Formation location	Type	Electrolyte salt	Solvent	Type	Content (wt %)			
1-18	Separator	PA1	$LiPF_6$	EC + DMC	Formula (1-4)	2	66	76	0.6
1-19					Formula (1-16)	2	66	78	0.6
1-20					Formula (1-18)	2	68	77	0.6
1-21					Formula (1-32)	2	67	76	0.6
1-22		PVDF + Al_2O_3	$LiPF_6$	EC + DMC	Formula (1-4)	2	68	78	0.5
1-23					Formula (1-16)	2	68	78	0.5
1-24					Formula (1-18)	2	66	76	0.5
1-25					Formula (1-32)	2	68	77	0.5
1-26		PA1	$LiPF_6$	EC + DMC	—	—	8	50	10
1-27		PA2					10	52	9
1-28		PVDF + Al_2O_3	$LiPF_6$	EC + DMC	—	—	5	60	5.5
1-29		PVDF + TiO_2					5	48	7
1-30		PVDF + SiO_2					6	50	5.5
1-31		PE	$LiPF_6$	EC + DMC	—	—	20	40	100
1-32					Formula (1-1)	2	18	39	100

In the case where the heat-resistant layer **27** contained PA1, Al_2O_3, or the like having a higher melting point or higher decomposition temperature than the melting point or the decomposition temperature of the separator **23**, the cycle retention ratio and the continuous charge retention ratio were increased, and the leak current was decreased according to presence or absence of the unsaturated cyclic ester carbonate in the electrolytic solution. The result shows that, in the case where the melting point or the like of the heat-resistant layer **27** is higher than the melting point or the like of the separator 23, and the electrolytic solution contains the unsaturated cyclic ester carbonate, short circuit is less likely to occur, and a decomposition reaction of the electrolytic solution is suppressed even under strict conditions such as continuous charge time.

In particular, in the case where the heat-resistant layer **27** had a higher melting point or the like and the electrolytic solution contained the unsaturated cyclic ester carbonate, the following advantageous tendencies were seen. Firstly, in the case where a polymer compound was used as a formation material of the heat-resistant layer **27**, if aromatic polyamide was used, a high cycle retention ratio and a high continuous charge retention ratio were obtained, and the leak current was kept low. Secondly, in the case where an oxide was used as a formation material of the heat-resistant layer **27**, if aluminum oxide was used, the cycle retention ratio and the continuous charge retention ratio were further increased, and the leak current was further decreased. Thirdly, in the case where the content of the unsaturated cyclic ester carbonate was from 0.1 wt % to 10 wt % both inclusive, a high cycle retention ratio and a high continuous charge retention ratio were obtained, and the leak current was kept low. In this case, in the case where the content thereof was from 1 wt % to 10 wt % both inclusive, and more specifically, the content thereof was from 2 wt % to 5 wt % both inclusive, the cycle retention ratio and the continuous charge retention ratio were further increased, and the leak current was further decreased.

In the case where the heat-resistant layer **27** contained PE having a lower melting point or lower decomposition temperature than the melting point or the decomposition temperature of the separator **23**, although the leak current was retained, the cycle retention ratio and the continuous charge retention ratio were decreased according to presence or absence of the unsaturated cyclic ester carbonate in the electrolytic solution. However, the leak current became an excessive value. The result shows that, in the case where the melting point or the like of the heat-resistant layer **27** is lower than the melting point or the like of the separator **23**, short circuit easily occurs under strict conditions such as continuous charge time. The result also shows that, in this case, even if the electrolytic solution contains the unsaturated cyclic ester carbonate, a decomposition reaction easily proceeds.

Examples 2-1 to 2-10

Secondary batteries were fabricated by a procedure similar to that of Example 1-5, except that the composition of the solvent was changed as illustrated in Table 3, and the respective characteristics were examined.

In this case, newly used solvents are as follows. As other unsaturated cyclic ester carbonate, vinylene carbonate (VC) was used. As halogenated ester carbonates, 4-fluoro-1,3-dioxolane-2-one (FEC), trans-4,5-difluoro-1,3-dioxolane-2-one (t-DFEC), and bis(fluoromethyl)carbonate (DFDMC) were used. As sultone, propene sultone (PRS) was used. As acid anhydrides, sulfopropionic anhydride (PSAH) was used.

The content of VC in the solvent was 2 wt %, the content of FEC, t-DFEC, or DFDMC in the solvent was 5 wt %, and the content of PRS or PSAH in the solvent was 1 wt %.

TABLE 3

Charging voltage (upper limit value): 4.2 V										
			Electrolytic solution							
	Heat-resistant layer					Unsaturated cyclic ester carbonate		Cycle retention	Continuous charge retention	Leak
Example	Formation location	Type	Electrolyte salt	Solvent		Type	Content (wt %)	ratio (%)	ratio (%)	current (mA)
2-1	Separator	PVDF +	$LiPF_6$	EC +	VC	Formula	2	80	88	0.5
2-2		Al_2O_3		DMC	FEC	(1-1)		78	84	0.5
2-3					t-DFEC			77	84	0.5
2-4					DFDMC			76	84	0.5
2-5					PRS			76	90	0.5
2-6					PSAH			82	94	0.5
2-7		PVDF +	$LiPF_6$	EC +	VC	—	—	40	65	5.5
2-8		Al_2O_3		DMC	FEC			45	60	10
2-9					t-DFEC			35	55	12
2-10					DFDMC			36	58	10

Even if the composition of the solvent was changed, high cycle retention ratios and high conservation retention ratios were obtained, and the leak currents were kept low. In particular, in the case where the electrolytic solution contained other unsaturated cyclic ester carbonate, the halogenated ester carbonate, the sultone, or the acid anhydride, the cycle retention ratio and the conservation retention ratio were further increased, and the leak current was further decreased.

Examples 3-1 to 3-3

Secondary batteries were fabricated by a procedure similar to that of Example 1-5 except that the composition of the electrolyte salt was changed as illustrated in Table 4, and the respective characteristics were examined.

In this case, newly used electrolyte salts were lithium tetrafluoroborate ($LiBF_4$), bis[oxalato-O,O']lithium borate (LiBOB) represented by Formula (8-6), and bis(trifluoromethanesulfonyl)imide lithium ($LiN(CF_3SO_2)_2$: LiTFSI). The content of $LiPF_6$ with respect to the solvent was 0.9 mol/kg, and the content of $LiBF_4$ or the like with respect to the solvent was 0.1 mol/kg.

TABLE 4

Charging voltage (upper limit value): 4.2 V										
			Electrolytic solution							
	Heat-resistant layer					Unsaturated cyclic ester carbonate		Cycle retention	Continuous charge retention	Leak
Example	Formation location	Type	Electrolyte salt		Solvent	Type	Content (wt %)	ratio (%)	ratio (%)	current (mA)
3-1	Separator	PVDF +	$LiPF_6$	$LiBF_4$	EC +	Formula	2	74	86	0.5
3-2		Al_2O_3		LiBOB	DMC	(1-1)		80	88	0.5
3-3				LiTFSI				78	88	0.4

Even if the composition of the electrolyte salt was changed, high cycle retention ratios and high conservation retention ratios were obtained, and the leak currents were kept low. In particular, in the case where the electrolytic solution contained other electrolyte salt such as $LiBF_4$, the cycle retention ratio and the conservation retention ratio were further increased, and the leak current was further decreased.

Examples 4-1 to 4-12 and 5-1 to 5-12

Secondary batteries were fabricated by a procedure similar to those of Examples 1-1 to 1-32 except that the upper limit value of the charging voltage was changed to 4.3 V or 4.4 V as illustrated in Table 5 and Table 6, and the respective characteristics were examined.

TABLE 5

Charging voltage (upper limit value): 4.3 V

	Heat-resistant layer		Electrolytic solution				Cycle retention ratio (%)	Continuous charge retention ratio (%)	Leak current (mA)
					Unsaturated cyclic ester carbonate				
Example	Formation location	Type	Electrolyte salt	Solvent	Type	Content (wt %)			
4-1	Separator	PA1	$LiPF_6$	EC + DMC	Formula (1-1)	2	65	75	1
4-2		PA2					60	72	1.2
4-3		PVDF + Al_2O_3					66	78	0.8
4-4		PVDF + TiO_2					62	71	1
4-5		PVDF + SiO_2					62	71	1
4-6		PA1	$LiPF_6$	EC + DMC	—	—	8	30	20
4-7		PA2					5	28	20
4-8		PVDF + Al_2O_3					5	40	15
4-9		PVDF + TiO_2					5	30	18
4-10		PVDF + SiO_2					5	38	16
4-11		PE	$LiPF_6$	EC + DMC	—	—	10	36	200
4-12					Formula (1-1)	2	8	34	150

TABLE 6

Charging voltage (upper limit value): 4.4 V

	Heat-resistant layer		Electrolytic solution				Cycle retention ratio (%)	Continuous charge retention ratio (%)	Leak current (mA)
					Unsaturated cyclic ester carbonate				
Example	Formation location	Type	Electrolyte salt	Solvent	Type	Content (wt %)			
5-1	Separator	PA1	$LiPF_6$	EC + DMC	Formula (1-1)	2	60	73	1.5
5-2		PA2					58	71	1.4
5-3		PVDF + Al_2O_3					62	76	1
5-4		PVDF + TiO_2					59	70	1.3
5-5		PVDF + SiO_2					59	70	1.3
5-6		PA1	$LiPF_6$	EC + DMC	—	—	8	20	30
5-7		PA2					4	20	32
5-8		PVDF + Al_2O_3					6	34	25
5-9		PVDF + TiO_2					5	30	28
5-10		PVDF + SiO_2					5	32	27
5-11		PE	$LiPF_6$	EC + DMC	—	—	12	30	250
5-12					Formula (1-1)	2	10	30	212

Even if the upper limit value of the charging voltage was increased, results similar to those of Table 1 and Table 2 were obtained. That is, in the case where the melting point or the decomposition temperature of the heat-resistant layer **27** was higher than the melting point or the decomposition temperature of the separator **23**, if the electrolytic solution contained the unsaturated cyclic ester carbonate, a high cycle retention ratio and a high continuous charge retention ratio were obtained, and the leak current was kept low. In this case, as the charging voltage was increased, the battery capacity was increased accordingly.

From the results of Table 1 to Table 6, in the case where the heat-resistant layer having a higher melting point or higher decomposition temperature than the melting point or the decomposition temperature of the separator was included at least in the region in which the cathode active material layer and the anode active material layer are opposed to each other between the cathode and the anode, and the electrolytic solution contained the unsaturated cyclic ester carbonate, superior battery characteristics were obtained.

The present application has been described with reference to the embodiment and Examples. However, the present application is not limited to the examples described in the embodiment and Examples, and various modifications may be made. For example, the description has been given of the lithium ion secondary battery as a secondary battery type. However, applicable secondary battery type is not limited thereto. The secondary battery of the present application is similarly applicable to a secondary battery in which the anode capacity includes a capacity due to inserting and extracting lithium ions and a capacity associated with precipitation and dissolution of lithium metal, and the battery capacity is expressed by the sum of these capacities. In this case, an anode material capable of inserting and extracting lithium ions is used as an anode active material, and the chargeable capacity of the anode material is set to a smaller value than the discharge capacity of the cathode.

Further, the description has been given with the specific examples of the case in which the battery structure is the cylindrical type or the laminated film type, and the battery device has the spirally wound structure. However, applicable structures are not limited thereto. The secondary battery of the present application is similarly applicable to a battery having other battery structure such as a square-type battery, a coin-type battery, and a button-type battery or a battery in which the battery device has other structure such as a laminated structure.

Further, the description has been given of the case using Li as an electrode reactant. However, the electrode reactant is not necessarily limited thereto. As an electrode reactant, for example, other Group 1 element such as Na and K, a Group 2 element such as Mg and Ca, or other light metal such as Al may be used. The effect of the present application may be obtained without depending on the electrode reactant type, and therefore, even if the electrode reactant type is changed, a similar effect is obtainable.

Further, with regard to the content of the unsaturated cyclic ester carbonate, the description has been given of the appropriate range derived from the results of Examples. However, the description does not totally deny a possibility that the content is out of the foregoing range. That is, the foregoing appropriate range is a range particularly preferable for obtaining the effects of the present application. Therefore, as long as the effects of the present application are obtained, the content may be out of the foregoing range in some degrees.

It is possible to achieve at least the following configurations from the above-described exemplary embodiment and the modifications of the disclosure.

(1) A secondary battery including:

a cathode and an anode that are opposed to each other with a separator in between; and

an electrolytic solution, wherein

the cathode includes a cathode active material layer on a cathode current collector,

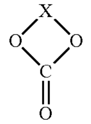
the anode includes an anode active material layer on an anode current collector,

a heat-resistant layer is provided at least in a region in which the cathode active material layer and the anode active material layer are opposed to each other between the cathode and the anode,

the heat-resistant layer includes a material having a higher melting point or higher decomposition temperature than a melting point or decomposition temperature of the separator, and

the electrolytic solution includes an unsaturated cyclic ester carbonate represented by the following Formula (1),

(1)



where X is a divalent group in which m-number of >C=CR1R2 and n-number of >CR3R4 are bonded in any order; each of R1 to R4 is one of a hydrogen group, a halogen group, a monovalent hydrocarbon group, a monovalent halogenated hydrocarbon group, a monovalent oxygen-containing hydrocarbon group, and a monovalent halogenated oxygen-containing hydrocarbon group; any two or more of the R1 to the R4 are allowed to be bonded to one another; and m and n satisfy $m \geq 1$ and $n \geq 0$.

(2) The secondary battery according to (1), wherein

the material having the higher melting point or the higher decomposition temperature than the melting point or the decomposition temperature of the separator is a polymer compound, and

the polymer compound includes one or more of polyamide, polystyrene, polymethyl methacrylate, polycarbonate, polyethylene terephthalate, polybutylene terephthalate, polyphenylene sulfide, polysulfone, polyethersulfone, polyether ether ketone, polytetrafluoroethylene, polyimide, polyether imide, melamine, benzoguanamine, and polytetrafluoroethylene.

(3) The secondary battery according to (1), wherein

the material having the higher melting point or the higher decomposition temperature than the melting point or the decomposition temperature of the separator is an oxide, and

the oxide includes one or more of aluminum oxide, titanium oxide, silicon oxide, and zirconium oxide.

(4) The secondary battery according to (3), wherein

the heat-resistant layer includes a retaining polymer compound retaining the oxide, and

the retaining polymer compound includes one or more of polyamide, polystyrene, polymethyl methacrylate, polycarbonate, polyethylene terephthalate, polybutylene terephthalate, polyphenylene sulfide, polysulfone, polyethersulfone, polyether ether ketone, polytetrafluoroethylene, polyimide, polyether imide, melamine, benzoguanamine, polytetrafluoroethylene, and polyvinylidene fluoride.

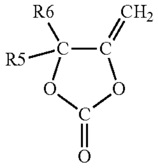
(5) The secondary battery according to any one of (1) to (4), wherein the heat-resistant layer is provided on the separator.

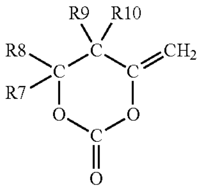
(6) The secondary battery according to any one of (1) to (5), wherein

the halogen group includes a fluorine group, a chlorine group, a bromine group, and an iodine group, and

the monovalent hydrocarbon group, the monovalent halogenated hydrocarbon group, the monovalent oxygen-containing hydrocarbon group, and the monovalent halogenated oxygen-containing hydrocarbon group include an alkyl group with carbon number from 1 to 12 both inclusive, an alkenyl group with carbon number from 2 to 12 both inclusive, an alkynyl group with carbon number from 2 to 12 both inclusive, an aryl group with carbon number from 6 to 18 both inclusive, a cycloalkyl group with carbon number from 3 to 18 both inclusive, an alkoxy group with carbon number from 1 to 12 both inclusive, a group obtained by bonding two or more thereof, and a group obtained by substituting each of part or all of hydrogen groups thereof by a halogen group.

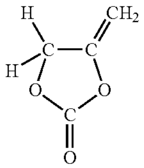
(7) The secondary battery according to any one of (1) to (6), wherein the unsaturated cyclic ester carbonate is represented by one of the following Formula (2) and the following Formula (3),

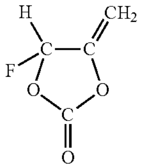

(2)

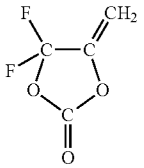

(3)

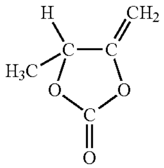
where each of R5 to R10 is one of a hydrogen group, a halogen group, a monovalent hydrocarbon group, a monovalent halogenated hydrocarbon group, a monovalent oxygen-containing hydrocarbon group, and a monovalent halogenated oxygen-containing hydrocarbon group; the R5 and the R6 are allowed to be bonded to each other; and any two or more of the R7 to the R10 are allowed to be bonded to one another.

(8) The secondary battery according to any one of (1) to (7), wherein the unsaturated cyclic ester carbonate is represented by one of the following Formula (1-1) to the following Formula (1-56),

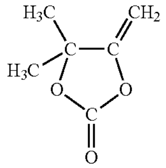

(1-1)

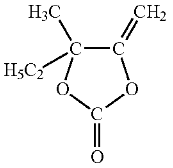

(1-2)

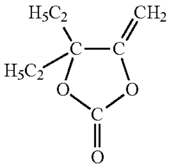

(1-3)

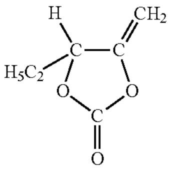

(1-4)

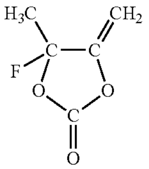
-continued

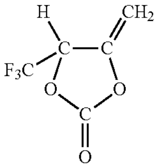

(1-5)

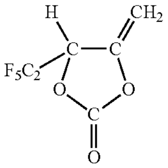

(1-6)

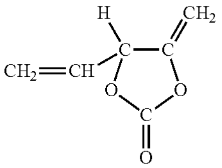

(1-7)

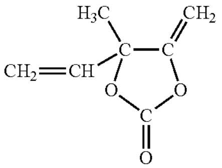

(1-8)


(1-9)


(1-10)

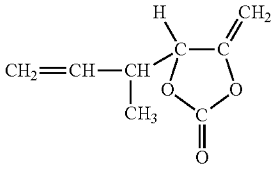

(1-11)


(1-12)

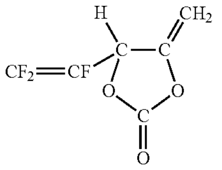

(1-13)

-continued

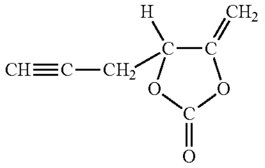
(1-14)



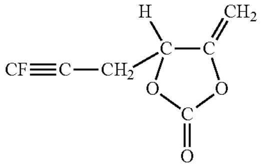
(1-15)



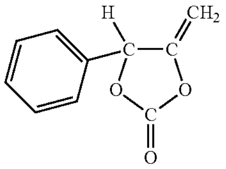
(1-16)



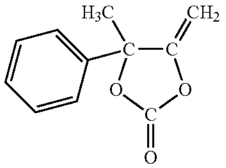
(1-17)



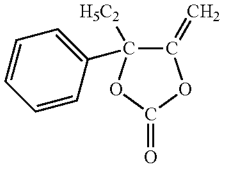
(1-18)



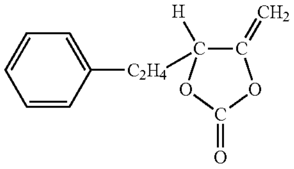
(1-19)



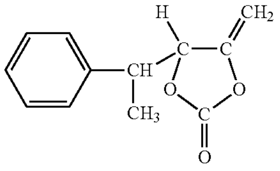
(1-20)



(1-21)

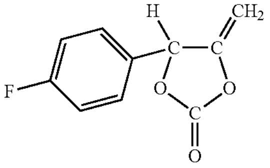


(1-22)

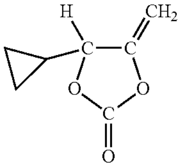


-continued

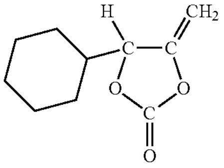
(1-23)



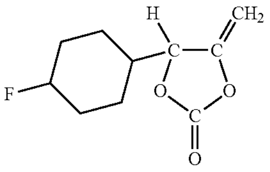
(1-24)



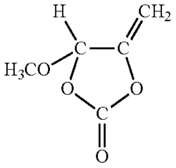
(1-25)



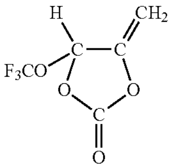
(1-26)



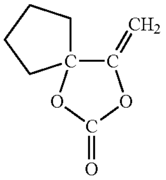
(1-27)



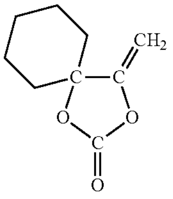
(1-28)



(1-29)

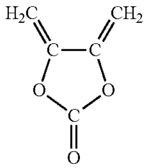


(1-30)

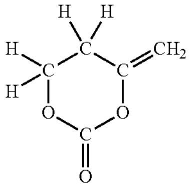


-continued

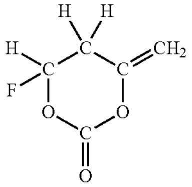
(1-31)



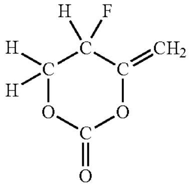
(1-32)



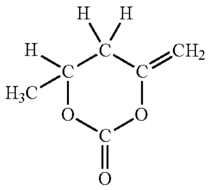
(1-33)



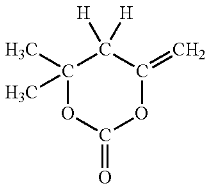
(1-34)



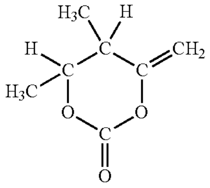
(1-35)



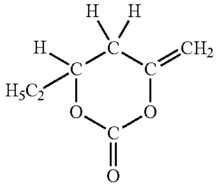
(1-36)



(1-37)

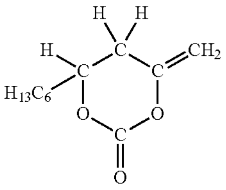


(1-38)

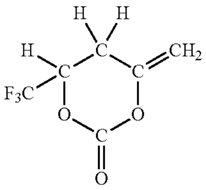


-continued

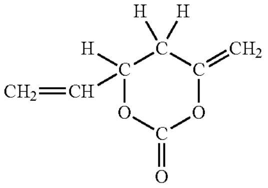
(1-39)



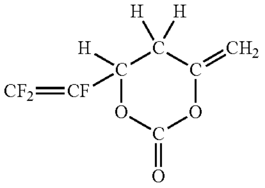
(1-40)



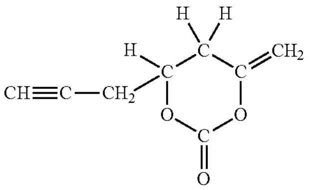
(1-41)



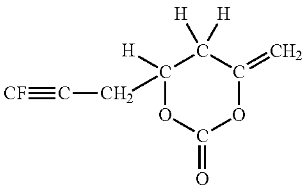
(1-42)



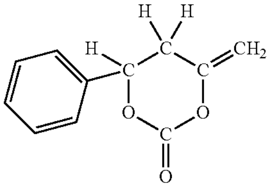
(1-43)



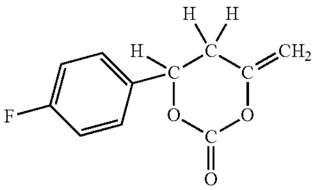
(1-44)



(1-45)

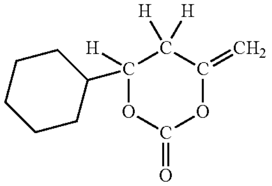


(1-46)

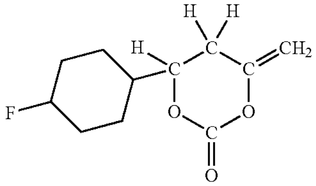


-continued

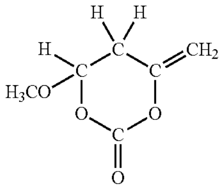
(1-47)



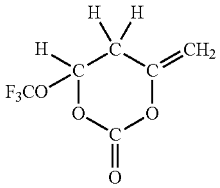
(1-48)



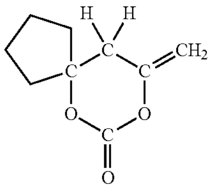
(1-49)



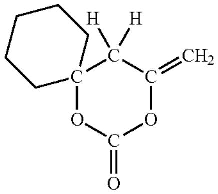
(1-50)



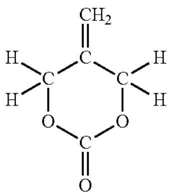
(1-51)



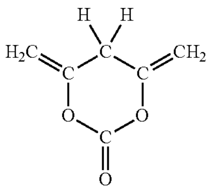
(1-52)



(1-53)

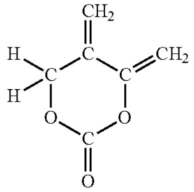


(1-54)

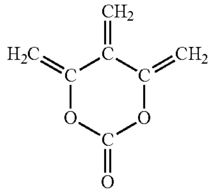


-continued

(1-55)



(1-56)



(9) The secondary battery according to any one of (1) to (8), wherein a content of the unsaturated cyclic ester carbonate in the electrolytic solution is from about 0.01 weight percent to about 10 weight percent both inclusive.

(10) The secondary battery according to any one of (1) to (9), wherein an open circuit voltage in a fully-charged state per a pair of the cathode and the anode is equal to or more than 4.3 volts.

(11) The secondary battery according to any one of (1) to (10), wherein the secondary battery is a lithium ion secondary battery.

(12) A battery pack including:

the secondary battery according to any one of (1) to (11);

a control section controlling a used state of the secondary battery; and

a switch section switching the used state of the secondary battery according to an instruction of the control section.

(13) An electric vehicle including:

the secondary battery according to any one of (1) to (11);

a conversion section converting electric power supplied from the secondary battery into drive power;

a drive section operating according to the drive power; and

a control section controlling a used state of the secondary battery.

(14) An electric power storage system including:

the secondary battery according to any one of (1) to (11);

one or more electric devices supplied with electric power from the secondary battery; and

a control section controlling the supplying of the electric power from the secondary battery to the one or more electric devices.

(15) An electric power tool including:

the secondary battery according to any one of (1) to (11); and

a movable section being supplied with electric power from the secondary battery.

(16) An electronic apparatus including the secondary battery according to any one of (1) to (11) as an electric power supply source.

It should be understood that various changes and modifications to the presently preferred embodiments described herein will be apparent to those skilled in the art. Such changes and modifications can be made without departing from the spirit and scope of the present subject matter and without diminishing its intended advantages. It is therefore intended that such changes and modifications be covered by the appended claims.

The invention is claimed as follows:

1. A secondary battery comprising:

a cathode and an anode that are opposed to each other with a separator in between; and

an electrolytic solution including a solvent and a salt, wherein

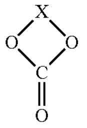
the cathode includes a cathode active material layer on a cathode current collector,

the anode includes an anode active material layer on an anode current collector,

a heat-resistant layer is provided on at least one side of the separator, and

the electrolytic solution includes an unsaturated cyclic ester carbonate represented by the following Formula (1),

(1)



where X is a divalent group in which m-number of >C═CR1R2 and n-number of >CR3R4 are bonded in any order; each of R1 to R4 is one of a hydrogen group, a halogen group, a monovalent hydrocarbon group, a monovalent halogenated hydrocarbon group, a monovalent oxygen-containing hydrocarbon group, and a monovalent halogenated oxygen-containing hydrocarbon group; any two or more of the R1 to the R4 are allowed to be bonded to one another; and m and n satisfy $m \geq 1$ and $n \geq 0$,

wherein the content of the unsaturated cyclic ester carbonate in the electrolytic solution is 5 wt % or less,

wherein the electrolyte solution further includes at least one selected from the group consisting of (a) a halogenated ester carbonate or a halogenated chain ester carbonate, and (b) a sultone,

wherein the heat-resistant layer further includes one or more of aluminum oxide, titanium oxide and zirconium oxide, having an average particle diameter ranging from 0.01 μm to 1 μm both inclusive,

wherein a thickness of at least one of the heat resistant layers is from 0.1 μm to 10 μm both inclusive, and

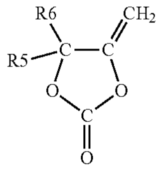
wherein a density of at least one of the heat-resistant layers is from 0.01 mg/cm^2 to 10 mg/cm^2 both inclusive.

2. The secondary battery according to claim **1**, wherein the halogen group includes a fluorine group, a chlorine group, a bromine group, and an iodine group, and

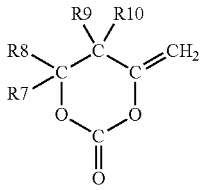
the monovalent hydrocarbon group, the monovalent halogenated hydrocarbon group, the monovalent oxygen-containing hydrocarbon group, and the monovalent halogenated oxygen-containing hydrocarbon group include an alkyl group with carbon number from 1 to 12 both inclusive, an alkenyl group with carbon number from 2 to 12 both inclusive, an alkynyl group with carbon number from 2 to 12 both inclusive, an aryl group with carbon number from 6 to 18 both inclusive, a cycloalkyl group with carbon number from 3 to 18 both inclusive, an alkoxy group with carbon number from 1 to 12 both inclusive, a group obtained by bonding two or more thereof, and a group obtained by substituting each of part or all of hydrogen groups thereof by a halogen group.

3. The secondary battery according to claim **1**, wherein the unsaturated cyclic ester carbonate is represented by one of the following Formula (2) and the following Formula (3),

(2)



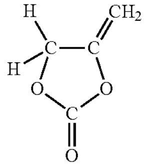
(3)



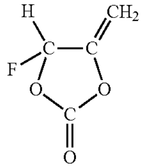
where each of R5 to R10 is one of a hydrogen group, a halogen group, a monovalent hydrocarbon group, a monovalent halogenated hydrocarbon group, a monovalent oxygen-containing hydrocarbon group, and a monovalent halogenated oxygen-containing hydrocarbon group; the R5 and the R6 are allowed to be bonded to each other; and any two or more of the R7 to the R10 are allowed to be bonded to one another.

4. The secondary battery according to claim **1**, wherein the unsaturated cyclic ester carbonate is represented by one of the following Formula (1-1) to the following Formula (1-56),

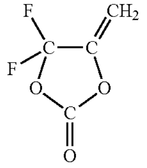
(1-1)



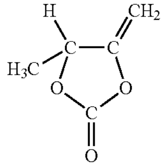
(1-2)



(1-3)

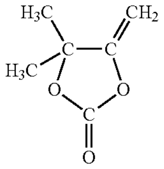


(1-4)

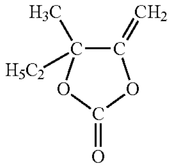


-continued

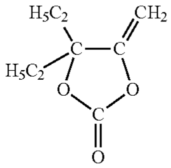
(1-5)



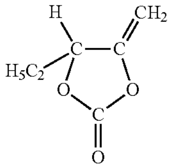
(1-6)



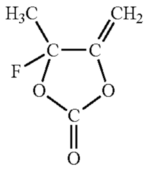
(1-7)



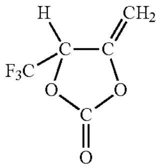
(1-8)



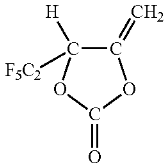
(1-9)



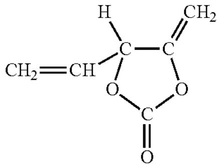
(1-10)



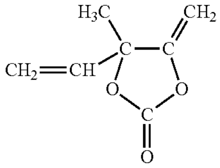
(1-11)



(1-12)

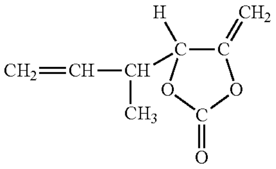


(1-13)

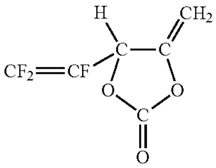


-continued

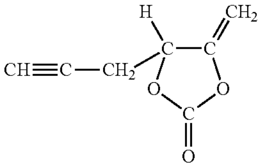
(1-14)



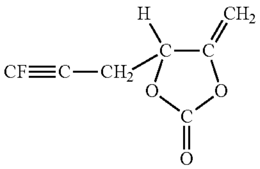
(1-15)



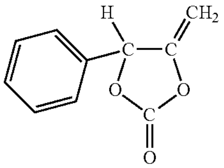
(1-16)



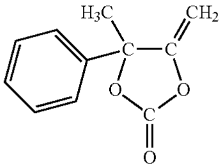
(1-17)



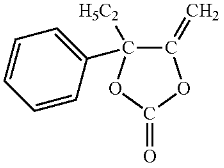
(1-18)



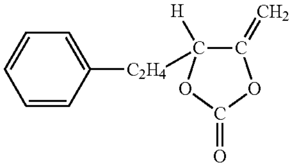
(1-19)



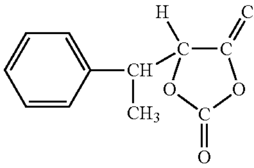
(1-20)



(1-21)

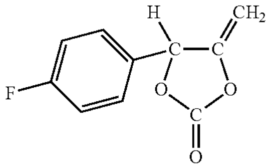


(1-22)

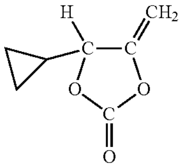


-continued

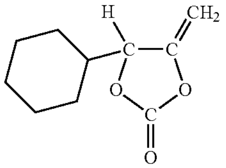
(1-23)



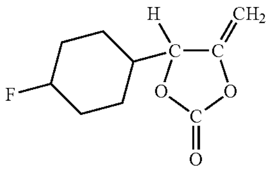
(1-24)



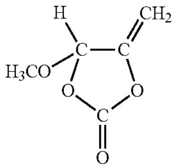
(1-25)



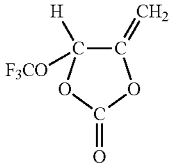
(1-26)



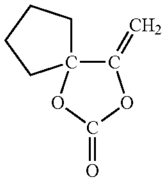
(1-27)



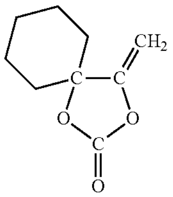
(1-28)



(1-29)

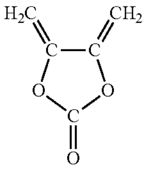


(1-30)

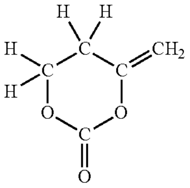


-continued

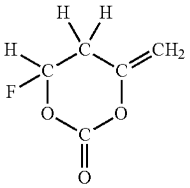
(1-31)



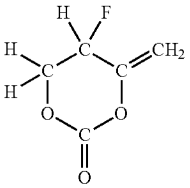
(1-32)



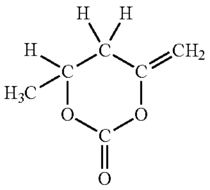
(1-33)



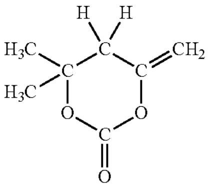
(1-34)



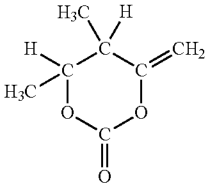
(1-35)



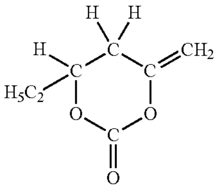
(1-36)



(1-37)

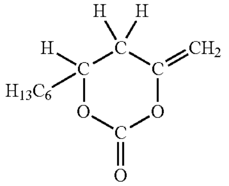


(1-38)

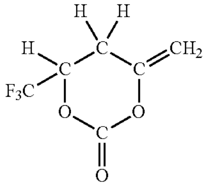


-continued

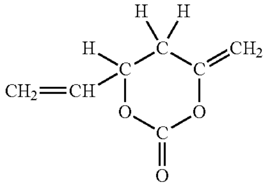
(1-39)



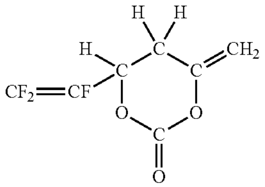
(1-40)



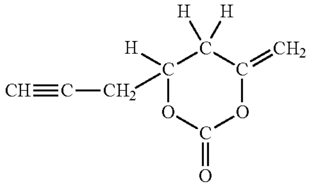
(1-41)



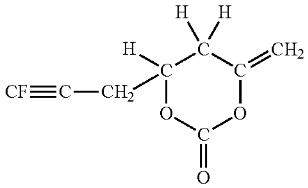
(1-42)



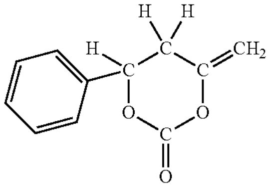
(1-43)



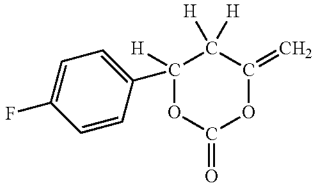
(1-44)



(1-45)

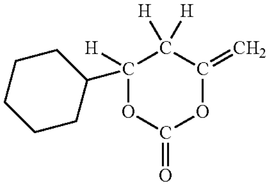


(1-46)

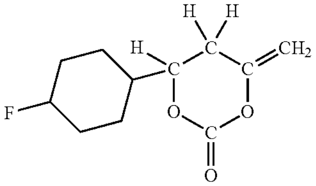


-continued

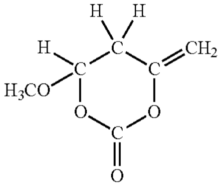
(1-47)



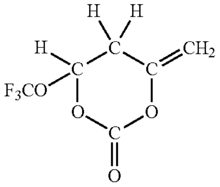
(1-48)



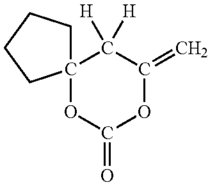
(1-49)



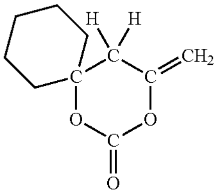
(1-50)



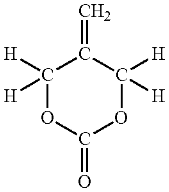
(1-51)



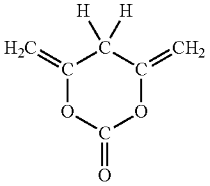
(1-52)



(1-53)

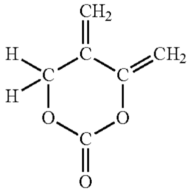


(1-54)

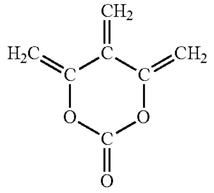


-continued

(1-55)



(1-56)



5. The secondary battery according to claim **1**, wherein the secondary battery is a lithium ion secondary battery.

6. A battery pack comprising:

a secondary battery;

a control section controlling a used state of the secondary battery; and

a switch section switching the used state of the secondary battery according to an instruction of the control section, wherein

the secondary battery includes

a cathode and an anode that are opposed to each other with a separator in between, and

an electrolytic solution including a solvent and a salt,

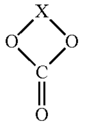
the cathode includes a cathode active material layer on a cathode current collector,

the anode includes an anode active material layer on an anode current collector,

a heat-resistant layer is provided on at least one side of the separator, and

the electrolytic solution includes an unsaturated cyclic ester carbonate represented by the following Formula (1),

(1)



where X is a divalent group in which m-number of >C=CR1R2 and n-number of >CR3R4 are bonded in any order; each of R1 to R4 is one of a hydrogen group, a halogen group, a monovalent hydrocarbon group, a monovalent halogenated hydrocarbon group, a monovalent oxygen-containing hydrocarbon group, and a monovalent halogenated oxygen-containing hydrocarbon group; any two or more of the R1 to the R4 are allowed to be bonded to one another; and m and n satisfy $m \geq 1$ and $n \geq 0$,

wherein the content of the unsaturated cyclic ester carbonate in the electrolytic solution is 5 wt % or less,

wherein the electrolyte solution further includes at least one selected from the group consisting of (a) a halogenated ester carbonate or a halogenated chain ester carbonate, and (b) a sultone,

wherein the heat-resistant layer further includes one or more of aluminum oxide, titanium oxide and zirconium oxide, having an average particle diameter ranging from 0.01 μm to 1 μm both inclusive,

wherein a thickness of the heat resistant layer ranges from 0.1 μm to 10 μm both inclusive, and

wherein a density of the heat-resistant layer ranges from 0.01 mg/cm^2 to 10 mg/cm^2 both inclusive.

7. The secondary battery according to claim **1**, wherein the heat-resistant layer includes at least one of polyamide, polystyrene, polymethyl methacrylate, polycarbonate, polyethylene terephthalate, polybutylene terephthalate, polyphenylene sulfide, polysulfone, polyethersulfone, polyether ether ketone, polytetrafluoroethylene, polyimide, polyether imide, melamine, benzoguanamine, polytetrafluoroethylene, and polyvinylidene fluoride.

8. The secondary battery according to claim **1**, wherein the heat-resistant layer includes benzoguanamine.

9. The secondary battery according to claim **1**, wherein the thickness of the at least one of the heat resistant layers is from 0.5 μm to 5 μm both inclusive.

10. The secondary battery according to claim **1**, wherein the halogenated ester carbonate is at least one of 4-fluoro-1,3-dioxolane-2-one (FEC), trans-4,5-difluoro-1,3-dioxolane-2-one (t-DFEC), and bis(fluoromethyl)carbonate (DFDMC),

the halogenated chain ester carbonate is at least one of fluoromethyl methyl carbonate, bis(fluoromethyl) carbonate, and difluoromethyl methyl carbonate,

the sultone is propane sultone or propene sultone, or

the acid anhydride is at least one of a carboxylic anhydride, a disulfonic anhydride, and a carboxylic acid sulfonic acid anhydride.

11. The secondary battery according to claim **10**, wherein the carboxylic anhydride is at least one of a succinic anhydride, a glutaric anhydride, and a maleic anhydride,

the disulfonic anhydride is an ethane disulfonic anhydride and a propane disulfonic anhydride, or

the carboxylic acid sulfonic acid anhydride is at least one of a sulfobenzoic anhydride, a sulfopropionic anhydride (PASH), and a sulfobutyric anhydride.

12. The secondary battery according to claim **1**, wherein the content of the sultone is from 0.5 wt % to 5 wt % both inclusive.

13. The secondary battery according to claim **1**, wherein the content of the acid anhydride is from 0.5 wt % to 5 wt % both inclusive.

14. The secondary battery according to claim **1**, wherein the electrolyte solution further includes at least one of 1,2-dimethoxyethane, tetrahydrofuran, 2-methyltetrahydrofuran, tetrahydropyran, 1,3-dioxolane, 4-methyl-1,3-dioxolane, 1,3-dioxane, 1,4-dioxane, N,N-dimethylformamide, N-methylpyrrolidinone, N-methyloxazolidinone, N,N'-dimethylimidazolidinone, nitromethane, nitroethane, sulfolane, trimethyl phosphate, and dimethyl sulfoxide.

15. The secondary battery according to claim **1**, wherein the salt comprises at least one of lithium hexafluorophosphate ($LiPF_6$), lithium tetrafluoroborate ($LiBF_4$), lithium perchlorate ($LiClO_4$) and lithium hexafluoroarsenate ($LiAsF_6$).

16. The secondary battery according to claim **15**, wherein the salt comprises both of hexafluorophosphate ($LiPF_6$) and lithium tetrafluoroborate ($LiBF_4$).

* * * * *